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LIGHTWEIGHT (COLD-DRY) INSULATED FOOTWEAR

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Uniroyal, Incorporated

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13. ABSTRACT

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Computerized studies were conducted to evaluate materials (polyols, isocyanates, and chain extenders) and formulations.

To fabricate the boot parts, liquid-injection molding type equipment was used.

Four pair of prototype footwear were fabricated.

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TECHNICAL REPORT

74-11-CE

LIGHTWEIGHT, (COLD-DRY) INSULATED FOOTWEAR

BY

E.J. KOPKA

UNIROYAL, INC.
MIDDLEBURY, CONNECTICUT

CONTRACT NO. #DAAG17-71-C-0070

Project Reference:
1J662713DJ40

Series: C&PLSEL-120

JULY 1973

Clothing and Personal Life Support Equipment Laboratory
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts

FOREWORD

The standard white insulated U.S. Army boots developed for cold-dry conditions weigh approximately 48 ounces per boot. Studies of energy consumption of the combat soldier indicate that one ounce of weight carried on the foot is equivalent to six ounces carried on the back and therefore a pair of 96 ounce boots are equivalent to 36 pounds.

To achieve a significant reduction in weight, it was necessary to make full use of advances in materials technology that have occurred since the development of the standard insulated U.S. Army footwear. The proposed footwear should be in the weight range of 24-26 ounces per boot (size 9R). This insulated lightweight footwear was also to be impermeable (water absorption maximum weight gain 5%) and offer maximum environmental protection down to -45°F, for periods of up to two hours of inactivity.

This report describes the work performed during the 25 month period from 15 January 1971 to 15 February 1973, under the supervision of Project Officer Joseph E. Assaf, U.S. Army Natick Laboratories, and covers the materials and processing studies and the fabrication of experimental lightweight polyurethane insulated footwear, using liquid injection molding equipment, performed by Uniroyal, Inc., Middlebury, Connecticut under Project Reference 1J662713DJ40 through Contract DAAG17-71-C-0070.

The Project Officer wishes to acknowledge Dr. Malcolm C. Henry, Deputy Director of the Clothing and Personal Life Support Equipment Laboratory (C&PLSEL) for his valued suggestions, and the aid and guidance of Mr. Douglas S. Swain, Footwear Technologist at NLABS, relative to design considerations.

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ABSTRACT

An upper boot foam and outsole foam were developed for a non-discoloring, cold-dry, off-white combat boot. The urethane foam used is flexible down to -45°F, closed-cell, and lightweight.

Computerized studies were conducted to evaluate materials (polyols, isocyanates, and chain extenders) and formulations.

To fabricate the boot parts, liquid-injection molding type equipment was used.

Four pair of prototype footwear were fabricated.

INTRODUCTION

In this study conducted by Uniroyal Inc., a number of urethane polymer systems were evaluated and tested with the objective being the development of a lightweight (24 oz. per boot), non-discoloring, impermeable (maximum water absorption 5%), insulated (for service down to -45°F), off-white combat boot.

Three computerized studies were conducted to evaluate materials (polyols, isocyanates, and chain extenders) and formulations. A combination of PTMG, hydrogenated MDI, and 1,4 butanediol showed the desired physical properties. Optimization of foam formulations based on those ingredients were made using water and Nitrosan as expanding agents.

Four prototype pair of boots were fabricated using the optimized formulations processed on a modified Polyair casting machine. The prototype boots were sprayed with a one-component coating, but development of a good quality, sprayable, one-component outer skin was not completed.

Of significant note were the development of a non-discoloring, closed-cell, flexible foam, the development of injection-moldable MDI type and HMDI type foams, and the fabrication of prototype footwear which met the main contract objectives.

Section I - Materials Studies

A. Original Candidate Selection

The objectives of the study were to develop a white, cold-dry, insulated boot which would be flexible down to -45°F, be non-discoloring, and be comparable to the black, lightweight-insulated boot in regards to physical properties and insulation.

The search for urethane materials to meet these objectives began with a literature survey, and was confined to commercially available raw materials. The articles searched included Chemical Abstracts, and various journals, patents, and commercial literature. These articles are numbered and listed in Appendix C entitled "Bibliography and References".

In examining the literature, each component constituting a polyurethane system was examined independently so that the best overall systems meeting the project objectives could be synthesized. A polyurethane system consists of three basic components - a polyol, a diisocyanate, and a chain extender. A polyol is usually a low molecular weight polymer (1000 to 3000 M.W.) and constitutes most of the polyurethane polymer backbone chain. The diisocyanate links the polyol segments end to end and these extended segments are further connected and formed into polymer chains by the chain extender.

The first step in examining the literature was to select polyols whose segments would be flexible enough to provide the polyurethane polymer with good low temperature flexibility. Examined literature indicated that several types of polyols had good low temperature flexibility, and these were hydroxy terminated polybutadienes and polyethers. (15, 32 - Appendix C)

Homopolymers of hydroxy terminated polybutadienes may be represented structurally as follows:

$$HO\left[-\left(CH_2-CH{=}CH-CH_2\right)_{0.2}-\left(CH_2-\underset{\displaystyle CH{=}CH_2}{\underset{|}{CH}}\right)_{0.2}-\left(CH_2-CH{=}CH-CH_2\right)_{0.6}-\right]_n OH$$

wherein the percent of cis, vinyl, and transisomers is 20%, 20% and 60% respectively; n may range from 44 - 75. Hydroxy terminated copolymers of butadiene with styrene or acrylonitrile may be represented schematically as follows:

$$HO\left[-\left(CH_2 - CH = CH - CH_2\right)_a - \left(\underset{X}{CH} - CH_2\right)_b\right]_n - OH$$

In the styrene butadiene copolymer, a is 0.75, b is 0.25 and X is a phenyl group. In the acrylonitrile-butadiene copolymer a is 0.85, b is 0.15 and X is a CN group; n may range from 40 - 50 for the styrene-butadiene copolymer and from 55 - 65 for the acrylonitrile-butadiene copolymer. Polyurethane systems made from polybutadiene polyols have indicated low temperature flexibility at -94°F. as measured by their brittle point. In relation to project objectives, stress-strain properties were low; however, die C tear was acceptable for the Poly BD based urethanes. Compression set and resilience was extremely good. These properties reflect those observed with polybutadiene rubber (32 - Appendix C)

Polyether type polyols may be represented by the following general formula:

$$HO\left[- R - O - R' -\right]_n OH$$

wherein R and R' may represent the same or different hydrocarbon segments. The molecular weight of the suitable polyether polyols ranges from 1,000 to 3,000. The literature has shown that the Clash-Berg low temperature modulus increase is low for polyether type polyurethanes - between -40° and -50°F. (15 - Appendix C). Also, polyether type polyurethanes have brittle points near -80°F and low temperature retraction (TR 10) temperatures at about -40°F. (16 - Appendix C)

Several diisocyanates, both discoloring and non-discoloring, were found to be suitable for evaluation with the above polyols. These included aliphatic types such as 1,6-hexamethylene diisocyanate (HDI), modified HDI and lysine methyl ester diisocyanate. Also included was a cycloaliphatic type, hydrogenated 4,4' diphenylmethane diisocyanate (HMDI). Other diisocyanates which were evaluated include tolylene diisocyanate (TDI), 4,4' diphenylmethane diisocyanaate (MDI) and diisocyanate mixtures such as Mondur HC (11 - Appendix C).

Aromatic diisocyanates (TDI or MDI) tend to produce polyurethane polymers which yellow or discolor in time. (11) Aliphatic and cycloaliphatic diisocyanates produce non-discoloring polyurethanes. These diisocyanates are less reactive than either TDI or MDI and normally require the use of a catalyst to increase their activity.

Materials like HDI are highly volatile and are modified to reduce their vapor pressure. The HDI is modified by reacting it with water so that the molecules are tied together to form a larger molecule.

The literature search also disclosed several chain extenders which could be used satisfactorily with the above polyols and diisocyanates. Included among these chain extenders were; N,N-bis (2 hydroxylpropyl) aniline; 1,4-butanediol; 1,6-hexanediol and trimethylhexanediol.

The described polyols, diisocyanates, and chain extenders which were evaluated initially are listed in Table I. Included in the table are the trade name, chemical name, source and equivalent weight of these materials; the equivalent weight is defined as the molecular weight divided by the functionality which is usually 2 for a diol or diisocyanate.

B. Preliminary Investigations

Several preliminary formulations were made using the materials listed in Table I. These formulations are listed in Table II. They were formulated and evaluated by using stress-strain screening tests to determine if the synthesis of the selected materials resulted in a feasible polyurethane system. The antioxidant and the UV absorber incorporated into the formulations were recommended in the technical literature on Poly Bd resins.

Based on the stress-strain data in Table II, the Hacconate H-12 appeared to be the better diisocyanate and Isonol C100 appeared to be the better chain extender.

The complete evaluation of four polyols (polybutadienes), seven diisocyanates and five chain extenders listed in Table I would have required 140 experiments to fully evaluate all of the materials and their interrelationship with each other. The situation was simplified by having statisticians devise a linear star statistical experimental design.

A linear star experimental design is used to approximate the values of a physical property by a linear equation. This equation describes the relationship of a physical property to the ingredients. For three variables or ingredients:

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3$$

TABLE I

LIST OF MATERIALS TO BE EVALUATED

MATERIAL	DESCRIPTION	EQUIVALENT WEIGHT	SOURCE
Polyols			
Poly BD R45M	Hydroxy Terminated Polybutadiene	1250	Arco Chemical Co.
Poly BD R15M	Hydroxy Terminated Polybutadiene	1430	Arco Chemical Co.
Poly BD CS15	Hydroxy Terminated Polybutadiene-Styrene-Copolymer	1540	Arco Chemical Co.
Poly BD CN15	Hydroxy Terminated Polybutadiene-Acrylonitrile Copolymer	1670	Arco Chemical Co.
Polymeg 650	Polytetramethylene Ether Glycol	315	Quaker Oats Co.
Polymeg 1000	Polytetramethylene Ether Glycol	520	Quaker Oats Co.
Polymeg 1500	Polytetramethylene Ether Glycol	760	Quaker Oats Co
Polymeg 2000	Polytetramethylene Ether Glycol	995	Quaker Oats Co.
Polymeg 3000	Polytetramethylene Ether Glycol	1450	Quaker Oats Co.
Isocyanates			
Isonate 143L	Modified MDI	143	UpJohn Co.
Nacconate H12	Hydrogenated MDI (70% Trans.)	131.2	Allied Chemical
Hylene W	Hydrogenated MDI (more than 30% Cis)	131.2	E.I. DuPont deNemours & CO.
Mondur HC (60%)	HDI - TDI mixture	371	Mobay Chemical Co
Desmodur N (75%)	Modified HDI	191	Mobay Chemical Co.
DDI 1410	Dimer Diisocyanate	300	General Mills Chemicals,Inc.
LDI (80%)	Lysine Methyl Ester Diisocyanate	99	Midland Div., Dexter Corp
TDI	Tolylene Diisocyanate	87	Mobay Chemical Co.
MDI	4,4'diphenylmethane diisocyanate	125	Mobay Chemical Co.
Reinforcing Polyols (Chain Extenders)			
Isonol C100	N,N-bis (2 Hydroxylpropyl) Aniline	104.5	UpJohn Co.
1,4 BD	1,4 - Butanediol	45	GAF Corp.
CHDM	1,4 - Cyclohexanedimethanol	73	Eastman Chemical Products
1,6 HD	1,6 - Hexanediol	59.1	Celanese Chemical Co
TMHD	Trimethylhexanediol	80.1	Hugo Stinnes Chemical Co.

TABLE II

PRELIMINARY COMPOUNDS FOR INITIAL SCREENING

Compound Number	103052	103054	103081	103083	103091	103092
Polyols						
R45M (Hydroxy Terminated Polybutadiene)	100	100	100	100	100	100
Isocyanates						
Isonate 143L (Modified MDI)	34.6					
Nacconate H12 (Hydrogenated MDI - 70% Trans)		31.6	31.6	31.6	31.6	31.6
Reinforcing Glycols						
Isonol C100 (N,N - bis 2 hydroxypropyl aniline)	16.8	16.8	16.8			
CHDM(1,4-cyclohexanedimethanol)				11.7	11.7	
1,4 BD (1,4-butanediol)						7.2
Superlite (antioxidant)	1.0	1.0	1.0	1.0	1.0	1.0
Tinuvin P (UV absorber)	1.0	1.0	1.0	1.0	1.0	1.0
Stannous Octoate (Catalyst)	0.3					
Dibutyltin Dilaurate (Catalyst)		2.0	2.0	0.5	0.5	0.5
Mold Temperature	220°F	120°F	155°F	155°F	180°F	180°F
Physicals						
Tensile	910	1550	1450	1140	780	770
100% Modulus	610	510	505	550	530	610
200% Modulus	-	680	660	860	700	770
300% Modulus	-	940	770	1050	-	-
400% Modulus	-	1020	915	-	-	-
% Elongation	180	500	590	330	230	200
Shore A Hardness	76	80	80	79	79	82

where: Y = the response (i.e., tensile strength, etc.)

X_1, X_2, X_3 = three ingredients

b_o, b_1, b_2, b_3 = the coefficients (constants)

The basis for fitting an equation of the type given above to a statistical design rests on the configuration of the design. The linear star design considers each variable at two levels.

This design was set up in the following manner. Three groups of ingredients were considered: 4 polyols, 7 isocyanates and 5 chain extenders. Each ingredient was considered at two levels (i.e., either some or none of the ingredient was to be used). One ingredient from each of the three groups was selected and used in an experiment. Two replicates of this experiment were run to measure reproducibility. These experiments were used as the "control" and to measure the effect each ingredient had on the physical properties.

Three experiments were then run which changed the polyol while keeping the control isocyanate and control chain extender fixed. Six experiments were run which changed the isocyanate while keeping the control polyol and control chain extender fixed. Four experiments were run which changed the chain extender while keeping the control polyol and control isocyanate fixed. Finally, additional experiments were run to measure reproducibility.

The assumption made is that the type of effect on the ingredients used in the "control" experiment resulting from using each of the ingredients from one group will be similar to the effect on the other ingredients from the two other groups. This design reduced the number of experiments from 140 to 22.

The experimental design is listed in Table III. Each number in a block designates a particular experiment performed. The numbers indicate the order in which the experiments were performed. For example, the first polyurethane system to be synthesized in this experiment included Poly BD R15M as the polyol, Mondur HC as the diisocyanate and 1,4-cyclohexanedimethanol as the chain extender. All 22 compounds were synthesized in this manner. Stress-strain measurements, low temperature (-45°F) modulus and Gehman tests were performed on each sample. This physical data was analyzed with the aid of a computer which established trends in relating the stress-strain data and low temperature flexibility to the evaluated polyols, diisocyanates and chain extenders.

TABLE III

LINEAR STAR STATISTICAL EXPERIMENTAL DESIGN #1

	POLY BD R 15 M							POLY BD R 45 M							POLY BD CS 15							POLY BD CN 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12							NAC H12							NAC H12						
CHDM	3 8 9	10	16	1 18 22	17	21	5	20							7 14 15							13						
ISONOL C 100	2																											
1,4-BD	6 11 19																											
1,6-HD	12																											
TMHD	4																											

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
Poly BD CS 15 - Hydroxy Terminated Styrene/Butadiene Copolymer
Poly BD CN-15 - Hydroxy Terminated Acrylonitrile/butadiene Copolymer
NAC H12 - Hydrogenated MDI (70% Trans)
Iso 143L - Modified MDI
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI Mixture (replaces Desmodur HL)
DES N - Modified HDI
DDI 1410 - Dimer Diisocyanates
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol
TMHD - Trimethylhexanediol

THE NUMBERS INDICATE THE ORDER IN WHICH THE EXPERIMENTS SHOULD BE RUN. EACH NUMBER IN ONE BOX INDICATES A SEPARATE EXPERIMENT.

C. Computerized Studies

1. Polybutadiene polyol - based formulations

The first of three computerized studies investigated the use of polybutadiene polyols, which are long-chain polyols, for maximizing low temperature flexibility. The twenty-two experiments necessary to evaluate the 140 combinations consisting of four polyols, five chain extenders and seven isocyanates were performed. The resulting samples were submitted for physical testing. The physical tests performed on these samples included stress/strain, Die C tear and Gehman low temperature flexibility. Based on the observed values, a regression analysis was made to develop equations to be used in predicting physical property values for all 140 combinations.

The predicted values for tensile strength, per cent elongation, Die C tear and Gehman low temperature flexibility are listed in Appendix A (Tables A-1 through A-6).

Any restriction can be made on the physical requirements to eliminate predicted values of combinations that will not meet the requirements. The following arbitrary restrictions were placed on the requirements: tensile strength, greater than or equal to 800 PSI; per cent elongation, greater than 200%; Gehman low temperature flexibility (T_5), less than -35°C; and Gehman (T_{10}), less than -60°C. These restrictions were used as a basis for the analysis of the data and the results are illustrated in Tables IV through VII.

Table IV illustrates the results obtained when the tensile strength is restricted to being greater than or equal to 800 PSI. Only four isocyanates - Nacconate H12, Mondur HC, Desmodur N and Hylene W, all of the polyols and all of the chain extenders met the requirements of tensile strength when the above restriction was placed upon them. Similar analyses can be made of remaining Tables V - VII. For example, Table VII shows that when the Gehman (T_{10}) requirement is applied (lower than -60°C), two polyols - Poly BD CS15 and Poly BD CN15, do not meet the requirement; however, more meaningful conclusions based on combinations which meet all the requirements will be discussed later.

All of the individual restrictions applied in Tables IV through VII can be applied simultaneously which results in Table VIII. Table VIII shows that only 16 combinations out of 140 met all of the restrictions simultaneously. Appendix A (Tables A-7 through A-10) lists the tensile strength, per cent elongation, Gehman (T_5) and Gehman (T_{10}) for all sixteen combinations which

TABLE IV

RESTRICTION: TENSILE STRENGTH $\geq$ 800 PSI

	POLY BD R 15 M							POLY BD R 45 M							POLY BD CS 15							POLY BD CN 15						
	HAC H12		HYLN W	MON MC	DES N			HAC H12		HYLN W	MON MC	DES N		LDI	HAC H12		HYLN W	MON MC	DES N		LDI	HAC H12		HYLN W				
CHDM			1045					960		1233					1088		1362	852	917					903				
ISONOL C 100	1050		1323	813	878			1238		1512	1002	1067		933	1367		1640	1130	1195		1065	908		1182				
1,4-BD	960		1233					1148		1422	912	977		847	1277		1550	1040	1105		975	818		1092				
1,6-HD			1023					938		1212					1067		1340	830	895					882				
TMHD	890		1163					1078		1352	842	907			1207		1403	970	1035		905			1022				

KEY:

Poly BD R15M - Hydroxy Terminated Polybutadiene
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HAC H12 - Hydrogenated MDI (70% Trans)
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Mon MC - MDI - TDI mixture (Replaces Mondur ML)
DES N - Modified HDI
DDI 1410 - Dimer Diisocyanates
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol
TMHD - Trimethylhexanediol

TABLE [illegible]

RESTRICTION: PERCENT ELONGATION > 200%

	POLY BD R 15M							POLY BD R 45 M						
	NAC H12		HYLN W			DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM								300		337			337	267
ISONOL C 100			217			217		317	213	253			353	283
1,4-BD	232		268			268		368	265	405	252	215	405	335
1,6-HD	210		247			247	377	347	243	383	230		383	313
TMHD	230		267			267		[illegible]	263	403	250	213	403	333

	POLY BD CS 15							POLY BD CN 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	287		333			333	263	350	247	387	233		387	317
ISONOL C 100	313	210	350			350	280	367	263	403	250	213	403	333
1,4-BD	365	262	402	248	212	402	332	418	315	455	302	265	455	385
1,6-HD	343	240	380	226		380	310	397	293	433	280	243	433	363
TMHD	363	260		247	210		330	416	313	453	300	263	453	383

KEY:

Poly BD R15 M	-	Hydroxy Terminated Polybutadiene
Poly BD R45 M	-	Hydroxy Terminated Polybutadiene
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DES N	-	Modified HDI
DDI 1410	-	Dimer Diisocyanates
LDI	-	Lysine Methyl Ester Diisocyanates
CHDM	-	1,4-Cyclohexanedimethanol
Isonol C100	-	N,N-bis(2 hydroxypropyl) Aniline
1,4-BD	-	1,4-Butanediol
1,6-HD	-	1,6-Hexanediol
TMHD	-	Trimethylhexanediol

TABLE VI

RESTRICTION: GERMAN $T_5 < -35°C$

	POLY BD R 15 M						POLY BD R 45 M						POLY BD CS 15		
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	LDI	NAC P12	ISO 143L	HYLN W	MON HC	DES N	LDI	ISO 143L	DES N	LDI
CHDM	65	-70	-62	-59	-70	-67	-54	-59	-51	-48	-59	-56	-40	-40	-37
ISONOL C 100	-51	-56	-48	-46	-56	-53	-40	-46	-38		-46	-43			
1,4-BD	-63	-69	-61	-58	-69	-66	-53	-58	-50	-47	-58	-55	-38	-38	
1,6-HD	-65	-70	-62	-60	-70	-67	-54	-60	-52	-49	-60	-57	-40	-40	-37
TMHD	-40	-45	-37		-45	-42									

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Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butenediol
1,6-HD - 1,6-Hexanediol
TMHD - Trimethylhexanediol

TABLE VII

RESTRICTION: GEHMAN T_{10} < -60°C

	POLY BD R 15 M							POLY BD R 45 M						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N		LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N		LDI
CHDM	-69	-70	-69	-67	-7[illegible]		-70	-68	-69	-68	-66	-69		-69
ISONOL C 100	-66	-67	-66	-64	-67		-67	-65	-65	-64	-62	-65		-65
1,4-BD	-68	-69	-68	-66	-69		-69	-67	-68	-67	-65	-68		-68
1,6-HD	-70	-71	-70	-68	-71		-71	-69	-69	-68	-66	-69		-69

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Isonol C100 - N,N-(2 hydroxypropyl) aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol

TABLE VIII

RESTRICTIONS: TENSILE STRENGTH ≥ 800 PSI; PERCENT ELONGATION 200%; ≥ GEHMAN $T_5 < -35°C$; GEHMAN $T_{10} < -60°C$

	POLY BD R 15 M							POLY BD R 45 M																				
	HAC H12		HYLN W					HAC H12		HYLN W	MON HC	DES W	LDI															
CHDM								20		X																		
ISONOL C 100			X					X		X			X															
1,4-BD	6 11 19		X					X		X	X	X	X															
1,6-HD			X					X		X																		

Numbers indicate compounds which were actually made and order in which they were made.
X's indicate compounds chosen by computer.

KEY:

Poly BD R 15 M	-	Hydroxy Terminated Polybutadiene
Poly BD R 45 M	-	Hydroxy Terminated Polyburadiene
HAC H12	-	Hydrogenated MDI (70% Trans)
CHDM	-	1,4 - Cyclohexanedimethanol
Isonol C100	-	N,N-bis(2 hydroxypropyl) Aniline
1,4-BD	-	1,4-Butanediol
1,6-HD	-	1,6-Hexanediol

TABLE IX

STATISTICAL ANALYSIS RESULTS

TEST	STD. ERROR OF Y	R^2 INDEX OF DETERMINATION	95% CONFIDENCE
Tensile Strength	74	.97	± 128
Percent Elongation	21	.98	± 42
Die C Tear	17	.99	± 34
100% Modulus	117	.72	± 234
200% Modulus	Not Enough Information to Make Analysis		
Gehman T_2	16	.76	± 32
Gehman T_5	6	.94	± 12
Gehman T_{10}	3	.98	± 6
Gehman T_{100}	2	.96	± 4

met all of the requirements. The data in these tables is a duplication of the values listed for these combinations in Tables A-1 through A-6.

Table IX has been included to illustrate the reliability and the accuracy of the results obtained in the statistical design experiment. For example, tensile strength is listed as having a standard error of Y equal to 74. This means that if a normal distribution curve is fitted to the tensile data, one standard deviation is equal to 74 units. The (R^2) index of determination for tensile strength is equal to .97. This figure means that 97% of the variation of points from the regression plot can be accounted for; 3% of the variation is unexplained. The last column of the table indicates that the 95% confidence for tensile strength is equal to $\pm$ 128. This figure indicates that within 95% confidence, the predicted values for tensile strength are no more than $\pm$ 128 units away from the true value. Each test listed in the table can be analyzed in a similar fashion.

In analyzing all the reported data, the following conclusions can be made for the combinations meeting all restrictions. The two best polyols for low temperature flexibility are Poly BD R15M and Poly BD R45M. The two best isocyanates which are also non-discoloring are Nacconate H12 and Hylene W. Chain extenders had little effect on low temperature flexibility; however, in respect to stress/strain properties, 1,4-Butanediol and 1,6-Hexanediol resulted in the best properties. An observed trend was that better low temperature flexibility varied directly with molecular weight; that is, low temperature flexibility increased with molecular weight so long as other variables remained constant. The entire experiment has shown that good low temperature flexibility but poor stress/strain properties result with the use of polybutadiene diols.

2. PTMG based formulations

The second set of experiments was designed to evaluate PTMG (Polytetramethylene ether glycol) and included the evaluation of isocyanates and chain extenders other than those used in the first set of experiments as well as the two isocyanates and three chain extenders selected from the first study. The experimental design, listed in Table X, required that twenty-seven experiments be performed to evaluate the eighty possible combinations.

The procedure used was identical to the one utilized for the first statistical design experiment. Data relating to the newly selected polyols, isocyanates and chain extenders which were evaluated in addition to those selected from the first statistical design experiment are listed in Table I.

TABLE X

LINEAR STAR STATISTICAL EXPERIMENTAL DESIGN #2

	POLYMEG 2000				POLYMEG 1000				POLYMEG 1500	POLYMEG 650	POLYMEG 3000			
	HYLN W	MDI	DES N	TDI	HYLN W	MDI	DES N	TDI	HYLN W	HYLN W	HYLN W	MDI	DES N	TDI
MDA* MOCA**	24 11 10	20 17 12	1	27	3	2	13	9 22 23	4	19	8	7 15 21	16	6
CHDM	26													
1,4-BD	14 5 25													
ISONOL C-100	18													

*MDA to be used with HYLN W and DES N. **MOCA to be used with MDI and TDI.

KEY:
- Polymeg 2000 - Polytetramethylene Ether Glycol (2000 mol.wt.)
- Polymeg 1000 - **Polytetramethylene Ether Glycol** (1000 mol.wt.)
- Polymeg 1500 - **Polytetramethylene Ether Glycol** (1500 mol.wt.)
- Polymeg 650 - **Polytetramethylene Ether Glycol** (650 mol.wt.)
- Polymeg 3000 - **Polytetramethylene Ether Glycol** (3000 mol.wt.)
- HYLN W - Hydrogenated MDI (more than 30% cis)
- MDI - 4,4'-diphenylmethane diisocyanate
- DES N - Modified HDI
- TDI - Tolylene diisocyanate
- MDA - p,p-Methylene dianiline
- MOCA - 3,3'-Dichloro-4,4'-diaminodi-phenylmethane
- CHDM - 1,4 - Cyclohexanedimethanol
- 1,4-BD - 1,4-Butanediol
- ISONOL C100 - N,N - bis (2 hydroxypropyl) Aniline

The numbers indicate the order in which the experiments should be run. Each number in a box indicates a separate experiment.

The PTMC polyol (Polymeg) was chosen because of its expected combination of good low temperature and stress/strain properties. This polyol was evaluated at five molecular weight levels ranging from 650 to 3,000 molecular weight. The selected isocyanates included nondiscoloring types - Hylene W and Desmodur N, selected from the first study. Two other isocyanates, TDI and MDI, were selected because of past experience in obtaining good physical properties with these isocyanates. In addition to CHDM, 1,4-BD and Isonol C100, two chain extenders, MDI and MOCA, were chosen because of anticipated improved physical properties based on past performance of these materials.

To describe the formulations and the method of preparation of the samples applicable to the 27 experiments, examples of the formulations, Samples No. 6 and 7, are listed below in parts per hundred of polyol by weight and their method of preparation follows:

Ingredient	Formulation No. 6	Formulation No. 7
Polymeg 3000	100	100
TDI	14.2	-
MDI	-	20.5
Dibutyl Tin Dilaurate	0.3	0.3
TMP	1.1	1.2
Dimethyl benzene	25	25
Cylohexanone	25	25
MOCA	9.2	9.2

In preparing the 27 samples, which include the two samples above, the following method was used. The PTMG (Polymeg 3000), isocyanate, dibutyl tin dilaurate and TMP (Trifunctional Polyol) are mixed together for approximately 5 minutes. To this mixture, dimethyl benzene and cylohexanone are added and mixed in. After mixing, the mixture is placed under vacuum to remove any dissolved gases. The chain extender (MOCA for Formulations No. 6 and 7) is then added and mixed thoroughly into the mixture. Immediately, this mixture is poured on a panel to form a film for testing. After the film has gelled, it is placed in an oven for two (2) hours at 150°F. The TMP was used with all samples in order to maintain equivalent molecular weight per crosslink in all film samples. The dibutyl tin dilaurate is a catalyst and was added to all samples to control the rate of reaction. The solvents are completely volatilized during the curing process and they had little or no effect on the overall physical properties of the compounds.

All 27 experiments were performed and the obtained samples were submitted for physical testing. Table XI lists all of the tests performed on the samples and the actual values obtained for each test. A regression analyses of the observed values was performed to develop equations based on these values for determining predicted values of physical properties for all of the 80 possible combinations.

Arbitrary restrictions were then placed on physical properties to eliminate combinations whose predicted value for a given physical property does not meet the arbitrary minimum value for that property. Table B-1 (Appendix B) lists the predicted values of the combinations meeting the single restriction of tensile strength being greater than or equal to 800 PSI. Similarly, Table B-2 lists the predicted values of those combinations meeting the single restriction of percent elongation being equal to or greater than 200%.

The placement of restrictions one at a time on all the possible combinations does not result in a highly selective means for determining desirable combinations of materials. It is not until a series of restrictions are applied simultaneously to all possible combinations that the resulting combinations can be further considered for fulfilling the objectives of a non-discoloring, durable, material for use in constructing lightweight insulated footwear. Therefore, several restrictions were applied simultaneously and the results in Table XII show all the combinations which meet the following simultaneously applied restrictions: tensile strength greater than or equal to 800 PSI; percent elongation, equal to or greater than 200%; and Gehman low temperature Flexibility (T_5) less than -35°C. Table XII shows that only 7 of the 80 possible combinations are satisfactory when the three above restrictions are applied simultaneously. The numbers appearing in the blocks of the diagram in Table XII list the actual experiments that were performed.

In further investigating the data developed for the combinations meeting all of the restrictions in Table XII, Tables B-3 - B-7 (Appendix B) list the 100% modulus, tensile strength, percent elongation, Die C tear and Gehman low temperature flexibility (T_5) for these combinations.

Table XIII was included and used to explain the reliability and accuracy of the results obtained in the Second Statistical Design Experiment. Table XIII shows the result of statistically fitting an equation to the test data. The values in the table illustrate how well the equation represents the data. For example, the Tensile data resulted in a standard error of 909 PSI, which is in large part due to poor reproducibility in results. This means there is 95% confidence ~~that~~ the actual test value does not vary from the value obtained in the equation by more than $\pm$ 1818 PSI, again due mainly to poor

TABLE XI

PHYSICAL TEST RESULTS OF THE 27 PREPARED SAMPLES

SAMPLE #	100% MODULUS LBS.	200% MODULUS LBS.	300% MODULUS LBS.	TENSILE STRENGTH PSI	PERCENT ELONGA-TION	DIE C TEAR LBS/IN.	GEHMAN (°C) T2	T5	T10	T100
1	180	-	-	330	110	30	-38	-52	-56	-70
2	735	980	1175	1175	300	434	- 8	-21	-28	-51
3	705	1105	1530	2320	430	420	+16	- 1	-15	-70
4	550	875	1380	4450	505	510	- 5	-29	-43	-70
5	210	370	530	2890	800	410	-20	-48	-58	-68
6	-	-	-	535	750	35	+24	+22	-43	-66
7	195	230	295	1740	950	235	+20	-45	-57	-70
8	400	780	1400	6700	520	565	+ 7	-10	-18	*
9	-	-	-	320	1000	70	+ 9	- 5	-12	-34
10	335	555	890	3390	650	460	-27	-48	-60	-70
11	360	650	1040	4550	590	500	-12	-42	-52	-70
12	235	355	470	1720	800	330	-19	-37	-43	-62
13	300	-	-	480	140	60	-15	-31	-40	-57
14	215	380	540	1560	750	245	-22	-41	-53	-66
15	90	180	235	1730	830	245	- 9	-45	-52	-70
16	240	-	-	425	180	140	+18	+ 1	-15	*
17	215	345	525	2480	800	320	-28	-42	-48	-68
18	-	-	-	9	1000	50	+ 6	-16	-27	-49
19	1210	1950	-	2100	210	395	+15	+ 5	-33	-70
20	235	390	555	3200	800	425	-29	-44	-50	-69
21	145	215	310	1840	940	295	-49	-55	-61	-70
22	-	-	-	280	950	90	+ 9	-10	-18	-39
23	-	-	-	430	1030	90				
24	265	445	670	3110	650	350	-10	-32	-46	-68
25	240	430	520	1490	760	300	- 8	-42	-54	-70
26	-	-	-	2	1000	30	+ 5	-30	-43	-65
27	-	-	-	450	1000	80	+ 5	-31	-40	-57

*Not Obtainable

TABLE XII

RESTRICTIONS: TENSILE STRENGTH $\geq$ 800 PSI; PERCENT ELONGATION $\geq$ 200%; GERMAN $T_5 \leq -35°C$

	POLYMEG 2000		POLYMEG 1500		POLYMEG 3000	
	HYLN W	MDI	HYLN W	MDI	HLYN W	MDI
MDA* MOCA**	24 11 10	20 17 12		X		7 15 21
1,4-BD	14 5 25		X		X	

*MDA to be used with HYLN W and DES N. **MOCA to be used with MDI and TDI.

KEY:
- Polymeg 2000 - Polytetramethylene Ether Glycol (2000 mol. wt.)
- Polymeg 1500 - Polytetramethylene Ether Glycol (1500 mol. wt.)
- Polymeg 3000 - Polytetramethylene Ether Glycol (3000 mol. wt.)
- HYLN W - Hydrogenated MDI (more than 30% cis)
- MDI - 4,4'-diphenylmethane diisocyanate
- MDA - p,p - .'ethylene dianiline
- MOCA - 3,3-Dichloro-4,4'-diaminodi-phenylmethane
- 1,4-BD - 1,4 - Butanediol

Numbers indicate compounds which were actually made and order in which they were made.
X's indicate compounds chosen by computer.

TABLE XIII

STATISTICAL ANALYSIS RESULTS

TEST	STANDARD ERROR OF Y	R^2 INDEX OF DETERMINATION	95% CONFIDENCE
Tensile Strength	909	.81	± 1818
Percent Elongation	141	.86	± 282
Die C Tear	73	.90	± 146
100% Modulus	114	.90	± 228
Gehman T_5	10	.80	± 20

reproducibility in results. This same equation has an R^2 of .81; meaning that the equation explains 81% of the actual variation in the data, leaving 19% unexplained. Gehman T_{10} data was not included because no significant correlation was found between the Gehman T_{10} results and the ingredients tested.

In analyzing all the reported data, the following conclusions can be made for the combinations meeting all restrictions. The two best polyols having good overall physical properties and good low temperature flexibility are PTMG-1500 and PTMG-2000. The two best isocyanates are Hylene W, a non-discoloring isocyanate and MDI, a discoloring isocyanate. The three best chain extenders were 1,4-Butanediol, MDA and MOCA. The entire experiment has shown that good stress strain properties and low temperature flexibility can be achieved with Polytetramethylene ether glycols.

3. Polybutadiene diol/PTMG blended formulations

A third study was performed with blends of PTMG-1500, PTMG-2000 and Polybutadiene Diol R15M wherein the blends contained 0%, 25%, and 50% of the PTMGs. These blends were prepared and reacted with Hylene W (isocyanate) and 1,4 - Butanediol (chain extender). The blend ratios and physical properties of these blends are listed in Table XIV.

These samples were not submitted for a third computerized study because the poorly developed physical properties listed in Table XIV suggested that high levels of Polybutandiene Diol seemed to act like a plasticizer, disrupting the molecular configuration of the polymer. However, low levels of Polybutadiene Diol (5 to 20%) were later added to PTMG formulations to determine if the Polybutadiene Diol would act as a "reacting plasticizer". This is discussed later in the text.

4. Optimization of the Formulations

Studies were performed using the one-shot method and the prepolymer method of developing an optimized formulation which would provide us with good overall physical properties, low-temperature flexibility and color stability.

In a one-shot method of preparing compound formulations, all ingredients are mixed together at the same time and random polymerization occurs with the formation of the polymer. To properly make a one-shot polyurethane, the proper use and selection of a catalyst is critical. In reporting the performed studies made with

TABLE XIV

FORMULATIONS AND PHYSICAL PROPERTIES OF DIOL BLENDS

	Samples				
Blend Ratio	A-1	A-2	A-3	A-4	A-5
Polymeg 1500	50				25
Polymeg 2000		25		50	
Polybutadiene Diol R15 M	50	75	100	50	75
Physical Properties					
100% Modulus (PSI)	280	70	245	230	235
300% Modulus (PSI)	520	170	-	470	-
Tensile Strength (PSI)	550	180	650	490	470
Percent Elongation (%)	310	380	215	320	210
Die C Tear(PPI)	145	80	175	160	175

a one-shot system, a single catalyst, dibutyl tin dilaurate, was the only catalyst used. To improve upon the reported results would require that a more complete catalyst study be performed.

Table XV lists all the compounds which were prepared by the one-shot method. The numbers, listed in parentheses alongside the parts of each ingredient added, indicate the order of addition of these ingredients. Besides determining the effect of the order of addition of ingredients, the B series was made to determine a method for preparing film samples which were clear and free of bubbles. The B series indicated that the best order of addition of ingredients was the method employed with sample B-3 and that clear films which were free from bubbles could be obtained by either using a Toluene/THF/dimethylbenzene solvent blend or a longer cure time. None of the B series films was submitted to Weatherometer or Fadeometer aging because these films were prepared without the use of pigments.

The C series of samples in Table XV was prepared by the one-shot method using an order of addition similar to B-3. This series was used to evaluate the effect of solvents and various titanium dioxide pigments on the properties of cast films. The series was performed also to evaluate the effect of the addition of a small amount of Polybutadiene R45M resin.

The data generated from the C series of samples indicated that the one-shot method of preparation does not result in consistent data. A possible explanation for this behavior is that the random polymerization associated with one-shot techniques is not a consistent means for producing a polyurethane polymer. Another observation was that the Polybutadiene R45M reduced physical properties in most cases. Also, different type pigments in identical compounds have little effect on the physical properties of a compound. Although the C series of samples did not discolor in the Weatherometer, unreacted ingredients migrated to the surface of the samples during the exposure time. Further studies were performed with the above ingredients with the ingredients combined to form polyurethane systems using the prepolymer or two-step method of preparation.

In the prepolymer method of preparation, the polyetherdiol is first reacted with the isocyanate (first step) to form the prepolymer and the isolated prepolymer is then further reacted with cross-linking agents to form the polyurethane polymer (second step). This method of preparation was utilized in preparing all the samples labeled W-1 through W-14 in Table XVI.

TABLE XV

PREPARED POLYURETHANE FORMULATIONS USING "ONE-SHOT" METHOD OF PREPARATION

	Samples									
Ingredients - PHR	B-1	B-2	B-3	C-1	C-2	C-3	C-4	C-5	C-6	Order of Ad C-Series
PTMG 2000	100 (1)*	100 (1)*	100 (1)*	100	100	100	100	100	100	1
Hylene W	29.9(2)	29.9(3)	29.9(4)	26.2	26.2	27.2	27.2	27.2	27.2	6
Dibutyl Tin Dilaurate	0.5(3)	0.5(4)	0.5(5)	0.5	0.5	0.5	0.5	0.5	0.5	7
TMP (Trimethylolpropane)	1.2(4)	1.2(5)	1.2(2)	1.2	2.7	1.2	1.2	1.2	2.7	2
1,4-Butanediol	4.5(5)	4.5(6)	4.5(3)	3.3	1.8	3.5	3.5	3.5	2.0	3
THF	-	10 (2)	-	-	-	-	-	-	-	
Dimethyl Benzene	-	10 (2)	-	-	-	-	-	-	-	
Toluene	-	10 (2)	-	-	-	-	-	-	-	
TiO_2 (HF-2 Cabot Corp.)	-	-	-	2.0	2.0	2.0	-	-	2.0	4
TiO_2 (R-202 E.I. duPont)	-	-	-	-	-	-	2.0	-	-	4
TiO_2 (R-771 New Jersey Zinc Co.)	-	-	-	-	-	-	-	2.0	-	4
Polybutadiene diol R45 M	-	-	-	-	-	5.0	5.0	5.0	5.0	5
Cure Temperature	200°F	200°F	R.T.	150°F	150°F	150°F	150°F	150°F	150°F	
Cure Time	2 hrs.	2 hrs.	5 hrs.	1.5 hrs.	1.5 hrs	1.5 hrs.	1.5 hrs.	1.5 hrs.	1.5 hrs.	
Post Cure Temperature	-	-	-	200°F	200°F	200°F	200°F	200°F	200°F	
Post Cure Time	-	-	-	2.5 hrs.	2.5 hrs.	2.5 hrs.	2.5 hrs.	2.5 hrs.	2.5 hrs.	
Film Appearance	Bubbles	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	
Physical Properties										
100% Modulus (PSI)	-	-	-	230	190	225	220	170	200	
300% Modulus (PSI)	-	-	-	390	400	430	410	315	-	
Tensile Strength (PSI)	1100	1850	3700	2400	925	900	2300	1750	375	
Percent Elongation (%)	650	950	600	530	410	420	550	630	215	
Die C Tear (PPI)	-	-	-	205	140	185	250	230	160	
Weatherometer (18 hrs. - No Filter)	-	-	-	Tacky	Tacky	Tacky	Tacky	Tacky	Tacky	

*Order of Addition - (B-Series)

TABLE XVI

PREPARED POLYURETHANE FORMULATIONS USING PREPOLYMER METHOD OF PREPARATION

Samples

Ingredients (PHR)	W-1	W-2	W-3	W-4	W-5	W-6	W-7	W-8	W-9	W-10	W-11	W-12	W-13	W-14
PTMG 2000	100	100	100	100	100	100	-	-	-	-	100	-	-	-
PTMG 3000	-	-	-	-	-	-	-	-	-	-	-	100	100	-
Adiprene LD 2699	-	-	-	-	-	-	100	100	100	100	-	-	-	-
Vibrathane B-602	-	-	-	-	-	-	-	-	-	-	-	-	-	100
Polybutadiene R45 M	-	-	-	-	13.5	-	-	10	20	30	-	-	-	-
Santicizer S-140	-	-	-	-	-	13.5	-	-	-	-	-	-	-	-
THF	-	-	68	34	34	34	25	25	25	25	34	34	34	40
Dimethyl Benzene	-	-	-	334	34	34	25	25	25	25	34	34	34	40
TiO_2 (Hilton-Davis)	-	1.2	1.2	1.2	1.2	1.2	1.0	1.0	1.0	1.0	2.7	2.7	2.7	10.0
Hylene W	-	-	-	-	-	-	-	-	-	-	35	229	-	-
Nacconate H 12	35	35	35	35	35	35	-	-	-	-	-	-	.29	-
Trimethylol Propane	1.2	1.2	1.2	1.2	1.1	1.2	0.9	0.9	0.8	0.8	1.3	1.3	1.3	-
1,4 Butanediol	5.5	5.5	5.5	5.5	5.4	5.5	4.2	3.9	3.6	3.4	5.7	5.4	5.4	-
Dibutyl Tin Dilaurate	-	-	-	-	-	-	0.5	0.5	0.5	0.5	-	-	-	-
mPDA	-	-	-	-	-	-	-	-	-	-	-	-	-	4.0
Cure Time Cure Temperature	1 hr. R.T.	1 hr. R.T.	1 hr. R.T.	1 hr. R.T.	1 hr. R.T.	1 hr. R.T.	1 hr. R.T.	1 hr. R.T	1 hr. R.T.	1 hr R.T.	1 hr. R.T	1 hr. R.T.	1 hr R.T.	1 hr. R.T.
Post Cure Time Post Cure Temperature	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F	2 hrs. 180°F

TABLE XVI

PREPARED POLYURETHANE FORMULATIONS USING PREPOLYMER METHOD OF PREPARATION (CONT'D)

Physical Properties	W-1	W-2	W-3	W-4	W-5	W-6	W-7	W-8	W-9	W-10	W-11	W-12	W-13	W-14
	Samples													
100% Modulus (PSI)	415	390	400	425	355	360	400	310	250	165	430	500	330	660
300% Modulus (PSI)	910	830	700	890	640	700	635	530	490	325	760	970	510	1000
Tensile Strength (PSI)	1950	2050	3500	4300	3900	4350	1850	4150	3700	3450	2700	3900	900	5300
Percent Elongation (%)	490	510	705	640	790	720	750	805	740	790	810	650	610	670
Die C Tear	400	355	420	455	425	400	335	355	300	245	460	535	270	545
Gehman Low Temperature (°C)														
T_2	-32.5	-36.5	-26.5	-33.5	-38	-36.5	-20.5	-30	-30	-28	-23	-	+20	-
T_5	-52.5	-52	-51.5	-54.0	-4	-53.5	-35.5	-43	-40	-41	-54	-11	+ 1	-
T_{10}	-61.5	-62.5	-62	-63.5	-69.5	-62.5	-43.5	-50	-48	-48	-65	-76	-	-
T_{100}	-	-	-	-	-	-	-67.5	-76.5	-68	-69	-70	-80	-80	-
Fadeometer (50 Hrs.)	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration
Weatherometer (50 Hrs. - No Filter)	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration	Slight Discoloration
Weatherometer (100 Hrs. With Filer)	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration	No Discoloration

The prepolymer used in preparing samples W-1 through W-6 was prepared from PTMG 2000 and Nacconate H12. The prepolymer was then cross-linked with 1,4 Butanediol. Further evaluations with this series included the determination of the effect of solvent on prepolymer systems, the effect of Polybutadiene R45M and the effect of Santicizer S 140 plasticizer on the prepolymer system. The data obtained from this series indicated that the prepolymer method of preparing films results in excellent films with good physical properties and low temperature flexibility. The use of solvent has no effect on these physical properties. The use of Polybutadiene R45M appears to improve low temperature flexibility without seriously affecting other physical properties.

Samples labeled W-7 through W-10 were prepared from Adiprene LD 2699 prepolymer. This prepolymer, not identified by its manufacturer, is believed to be a polytetramethylene ether glycol (PTMG) which is terminated with a non-discoloring isocyanate. This series of samples was prepared to evaluate Adiprene LD 2699, and to determine the optimum level of Polybutadiene R45M which could be added to improve low temperature flexibility, without seriously affecting other physical properties. The films made from this series of samples did not yield exceptional low temperature properties even though other physical properties were acceptable. The other conclusion derived from this data is that no further improvement in low temperature properties is derived from the Polybutadiene R45M when added in amounts greater than 10 parts per 100.

Samples labeled W-11 through W-14 were prepared so that a direct comparison could be made between PTMG 2000, PTMG 3000, and Vibrathane B-602. The data indicate that, although these prepolymers can have approximately equivalent physical properties, the PTMG 2000 results in samples having better low temperature flexibility.

D. Summary and Conclusions of the Material Studies

The objectives of this study were to develop a white, cold-dry insulated boot which would be flexible down to -45°F, be non-discoloring, and be comparable to the present standard black lightweight-insulated boot in regards to physical properties and insulation. To achieve these objectives, three computerized studies were run to develop the proper formulations. The first study investigated the use of polybutadiene polyols, which are long-chain polyols, for maximizing low temperature flexibility. Compounds based on these polyols had excellent low temperature properties, but other physical properties, such as stress-strain, were poor. In the second study, PTMG polyols were investigated as a means for maximizing low-temperature flexibility. The PTMG based compounds showed good low temperature properties, although not as good as the polybutadiene polyols, and good overall physical properties. The third study was an attempt to combine the excellent low temperature properties of the polybutadiene polyols with the good strength properties of the PTMG polyols. This study involved the blending of PTMG with polybutadiene polyol in varying ratios and physical testing of the resulting compounds. It was found that a 10% addition of polybutadienediol to PTMG improved the low temperature properties slightly while maintaining other physical properties. All other blended compounds were poor in low temperature properties and/or strength properties.

Besides evaluating polyols for low temperature properties, isocyanates were evaluated for non-discoloring properties and crosslinking agents for effect on overall physical properties.

The long-chain of the polyol effects the low temperature properties of the compound. To an extent, the longer the polymer chain the better the low temperature properties. Figure I shows the relationship of chain length (molecular weight) versus low temperature flexibility (Gehman data). It can be seen that compound based on a PTMG polyol of 2000 molecular weight has the best low temperature properties and that increasing the molecular weight to 3000 causes no improvement. Since PTMG 2000 based compounds also have good strength properties, any foam formulation should include PTMG 2000.

In selecting a non-discoloring isocyanate, it was known that aromatic diisocyanates such as tolylene diisocyanate (TDI) yield urethane polymers that tend to yellow on prolonged exposure to sunlight and such aromatic isocyanates should not be used in white boot formulations. This discoloration phenomena is believed by some to occur by oxidation of terminal aromatic amines, and by others, by the oxidation of the methylene group in urethane compounds derived from MDI. Some have tried to stabilize the urethane group against thermal degradation and yellowing by the addition of anti-oxidants or UV absorbers with limited success. Our studies have shown that a more desirable approach for achieving improved resistance to discoloration is by use of a cycloaliphatic diisocyanate instead of an aromatic diisocyanate. In fact, a compound based on hydrogenated MDI (either Hylene W-duPont or Nacconate H12 - Allied Chemical), a cyclo-aliphatic diisocyanate, is non-discoloring and was used in trial foam formulations. Since, however, aromatic diisocyanates are significantly different from aliphatic isocyanate with respect to reactivity and polymer compound preparation, a new series of parameters concerning foam formulations needed to be developed. This is discussed later.

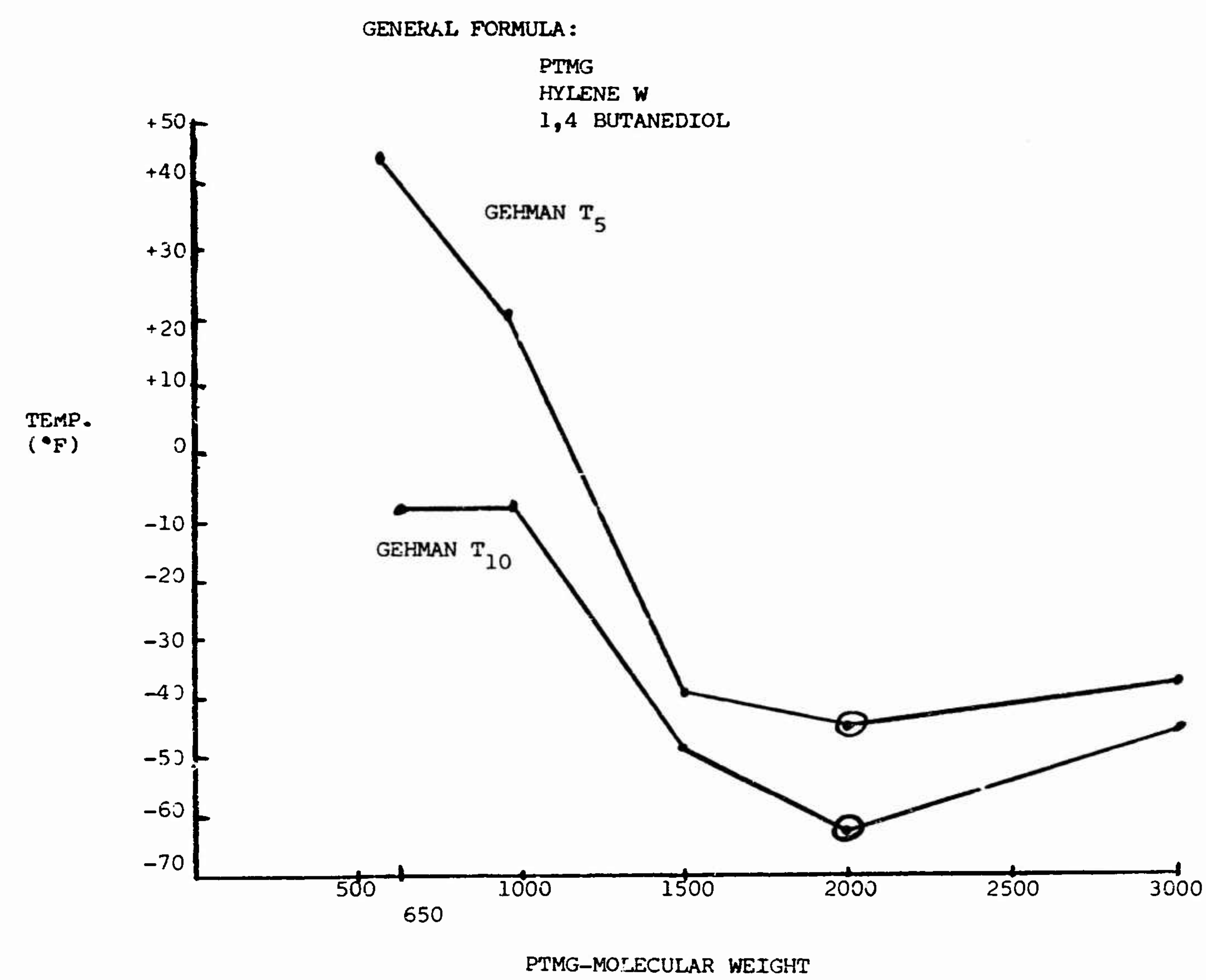

FIGURE 1 - VARIATION OF GEHMAN DATA VS. MOLECULAR WEIGHT OF PTMG POLYOLS

In making a urethane, an isocyanate is reacted with a polyol, sometimes using a crosslinking agent to control the physical properties of the resultant urethane compound. The three studies have shown that, of those cross-linking agents evaluated, 1,4 butanediol is the best cross-linking agent overall and should be used in any foam formulations.

Using PTMG 2000/hydrogenated MDI/1,4 butanediol based formulations, several trial foams were made and evaluated. When using the "one-shot" method to make foams or films (the C series of films), the compound failed to cure properly. Poor mixing or variable reactant reactivities may have been the cause, but in any case, the "one-shot" method did not process well. The prepolymer method for making foams processed well and the foams and films had good physical properties.

Section II - Compounding and Processing

A. Upper and Outsole Foam Formulations

1. Preliminary Analysis:

Six optimum formulations were chosen from the formulation studies in Phase I. Any of these six base formulations could have been used in Phase II to produce prototype boots. The major ingredients of the formulations were as follows:

Formulation	Polyetherdiol	Isocyanate	Chain Extender	Other Ingredients
No. 1	PTMG 2000	Hylene W	1,4 Butanediol	-----------
No. 2	PTMG 2000	Hylene W	1,4 Butanediol	Poly BD R45M (butadienediol)
No. 3	PTMG 2000	Hylene W	1,4 Butanediol	Santicizer S-140 (plasticizer)
No. 4	PTMG 2000	Nacconate H12	1,4 Butanediol	-----------
No. 5	PTMG 2000	Nacconate H12	1,4 Buutanediol	Poly BD R45M
No. 6	PTMG 2000	Nacconate H12	1,4 Butanediol	Santicizer S-140

In doing the original formulation studies, only cast polymer films were made from the formulations. To fabricate a prototype boot, one of the base formulations had to be modified to make (1) a urethane foam with 25-30 pound per cubic foot density for use as outsole material, (2) a second type of urethane foam with 8-12 pound per cubic foot density for use as upper boot material, and (3) a urethane sprayed film for use as a protective skin. The major portion of Phase II was spent developing urethane foam for the outsole and the upper.

To make an adequate foam, the foam formulations and processing techniques used should satisfy the following system requirements:

1. Proper gel time (too fast a gel induces tears and fissures; too lengthy a gel results in total foam collapse)

2. The gas evolution rate should be synchronized with polymer modulus build-up so that the cells do not coalesce nor fracture during expansion.

3. Equivalent activity of polyols and other ingredients at all stages of reaction to the isocyanate group, to ensure copolymerization at a rate controlled by the initial concentration of ingredients (to prevent bunching of low molecular weight additives).

4. Lowest possible viscosities of raw materials.

5. A cream time of 10 to 30 seconds.

6. Proper rise time and rise height (to insure optimum foam expansion).

7. A demold time of 2 to 15 minutes.

8. Stability of foam after demolding (minimum foam shrinkage and foam collapse).

9. Reproducibility of foam.

10. Formulation adaptable to available mixing and metering equipment.

The desired physical properties of the urethane foam are:

a. fine cell structure

b. predominantly closed cell

c. flexibility at room temperature and -45°F

d. good compressibility

e. toughness and durability

f. abrasion resistance

Three foaming methods can be employed to make the flexible foam to satisfy the above requirements. The methods are (1) the "one-shot" method, (2) the prepolymer method, and (3) the quasi-prepolymer method. In the one-shot method, all the components (polyol, isocyanate, surfactant, blowing agent, and catalyst) are combined at one time to form a foam, and the reaction is completed in "one-shot". If the use of the one-shot foaming method had become desirable, and since a metering and mixing machine for one-shot systems was not available for use, the prototype boots would have had to be made by hand-casting. However, hand-casted urethane films made in Phase I by this method, were usually of poor quality with inconsistent properties. The one-shot method, therefore, was not considered any further in Phase II as a means for making foam.

The prepolymer method involves the reaction of the hydroxyl compound with an excess of diisocyanate to form an isocyanate-terminated prepolymer. The prepolymer can then be mixed with the crosslinking agent, surfactant, blowing agent, and catalyst to make a "two-shot" foam. The prepolymer method has been successfully used to hand-cast urethane films in Phase I. One disadvantage to the prepolymer method is the necessity for accurate metering since the ratio of the prepolymer stream to the curing agent is 100 to 10. Inaccurate metering would create inconsistant and poor quality foam. If use of the prepolymer method had become desirable, suitable mixing and metering equipment (Mateer mixing machine and the Vichase machine) was available. Operation of the machine would have required considerable effort (adequate cleaning of machine parts, large amounts of materials, etc.), but the possibility of using the prepolymer technique was not ruled out.

The quasi-prepolymer method is a combination of the prepolymer and the one-shot techniques. The polyol component is prereacted with excess diisocyanate to form one component. Crosslinking agent, surfactant, blowing agent, and catalyst are mixed with additional polyol to form the second component. The two components are mixed, usually in equal quantities, to make reproducible, good quality foam. A Polyair liquid-injection-molding (LIM) machine was available on which the quasi-prepolymer technique could be used. Operation of the machine was relatively simple and only small amounts of raw materials were needed for processing. A major portion of the effort in Phase II was used to adapt an optimum formulation for processing on the LIM machine.

2. Prepolymer Preparation:

In both the prepolymer and the quasi-prepolymer methods, the initial stage is prepolymer preparation. The preparation of the prepolymer was approached from two angles. In the first approach, lab-size batches of prepolymer were made in gallon containers by adding the appropriate diisocyanate (Hylene W or Nacconate H12) to a sufficient quantity of PTMG 2000 to make a prepolymer with approximately 5% free NCO. Catalyst was added and the mixture was allowed to react 24 to 48 hours at 120°F. Another and better approach is to use a commercially-made prepolymer. DuPont had two prepolymers available which were suitable, LD-2699 and ECD-3056 prepolymer. Both materials were purported to be PTMG based with an aliphatic diisocyanate as the isocyanate portion. Both materials, then, would be non-discoloring, but the ECD-3056 was believed to be based on a longer-chain PTMG than the LD-2699 and hence would have the better low-temperature properties.

3. Hand-Cast Foam Samples

The first foam formulation based on LD-2699 prepolymer is listed in Table XVII as WF-1. Trimethylol-propane (TMP) is used in the formulation to keep the molecular weight per cross-link (M_c) of the polymer equal to 12,000. SF1079 is the surfactant, dibutyl tin dilaurate (DBTDL) is the catalyst, and Nitrosan is the blowing agent. Due to an excess amount of Nitrosan, WF-1 was overblown. The Nitrosan was reduced in WF-2, but the cream time of the system was too long. The catalyst was increased in WF-3 to reduce the cream time, but the system was still too slow. It was thought that a small amount of a hydroxyamine would increase the reaction rate sufficiently to allow proper foam formation. 0.5 gram of diethanolamine (DEA) was added in WF-4; however, the DEA caused bunching (and violation of requirement #3 mentioned previously). Stannous octoate (T9 catalyst) was added in WF-5 as another attempt to reduce the cream time, but the system was again too slow. Stannous octoate was increased to 2.0 grams in WF-6 resulting in a sufficiently fast system and a foam with course cell structure.

Evaluation of the lab-made prepolymer, based on PTMG 2000 and Hylene W was first done at the bench. Formulation WF-7 was tried, resulting in a fast system perhaps due to too much catalyst in the prepolymer. Temperatures of the components were lowered and no extra catalyst was added in WF-8, resulting in an excellent foam with a fine cell structure.

The preceding work was done using the prepolymer technique. The quasi-prepolymer technique was used in the following work. In formulation WF-9, Hylene W was added to the PTMG 2000/Hylene W prepolymer to reduce the viscosity and increase the amount of free NCO to 20%. PTMG 2000 was added to the hardener component (curing agent). A rigid foam resulted from the reaction of the two components. The reason for the rigidity can be found in the calculations. The formulation was calculated with regard to keeping the M_c at 12,000, but the percentage amounts of polyol, isocyanate, diol, and triol were not maintained. The

TABLE XVII

HAND-CAST FOAM SAMPLES

	WF-1	WF-2	WF-3	WF-4	WF-5	WF-6	WF-7	WF-8	WF-9	WF-10	WF-11	WF-12
LD-2699 Prepolymer	100	100	100	100	100	100	--	--	--	--	--	--
PTMG2000/Hylene W Prepolymer	--	--	--	--	--	--	100	100	38	38	38	38
Hylene W	--	--	--	--	--	--	--	--	62	39.7	39.7	39.7
TMP	0.9	0.9	0.9	0.9	0.9	0.9	1.0	1.0	2.0	1.5	1.5	1.5
1,4 Butanediol	4.2	4.2	4.2	4.2	4.2	4.2	4.3	4.3	16.0	6.5	6.5	6.4
PTMG 2000	--	--	--	--	--	--	--	--	75.0	85.1	85.1	85.0
Diethanolamine	--	--	--	0.5	--	--	--	--	--	--	--	--
SF 1079	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Nitrosan	3.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	--
Water	--	--	--	--	--	--	--	--	--	--	--	0.2
DBTDL catalyst	0.5	0.5	3.0	0.5	0.5	0.5	0.5	--	--	--	--	--
T-9 catalyst	--	--	--	--	0.5	2.0	--	--	--	--	--	0.5
Dabco catalyst	--	--	--	--	--	--	--	--	--	--	--	1.0
White pigment	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mold Temperature	--	--	--	--	215°F	215°F	--	215°F	215°F	215°F	215°F	215°F
Prepolymer Temperature	150°F	150°F	150°F	150°F	150°F	120°F	150°F	130°F	150°F	150°F	130°F	130°F
Hardener Temperature	150°F	150°F	150°F	150°F	150°F	100°F	150°F	130°F	150°F	150°F	130°F	130°F
Cream Time	long	long	long	--	long	good	fast	good	long	fast	good	good
Gel Time	--	--	--	too fast	--	good	fast	good	long	fast	good	good
Cell Structure	over blown	--	--	--	not uniform	course	--	fine	very course	course	course	course
Comments:	--	--	--	bunching	poor mixing	--	too much catalyst	--	rigid foam	high exotherm	use on LIM	use on LIM

actual percentage amounts of reactive ingredients in formulations WF-8 and WF-9 are as follows:

	WF-8	WF-9
PTMG 2000	70.3%	53.5%
Hylene W	24.7%	37.2%
1,4 Butanediol	4.3%	8.3%
TMP	1.0%	1.0%
	100.0%	100.0%

Formulation WF-10 is a modification of WF-9 reflecting the percentage amounts of ingredients as in WF-8. WF-10 resulted in a fast system with high exotherm. The temperatures of the components were lowered in WF-11 and good foam was made. Formulation WF-11 is suitable for use in the Polyair LIM machine. Formulation WF-12 differs from WF-11 in that it contains water as the blowing agent. Benchwork with WF-12 shows that this formulation is also suitable for use in the LIM machine.

4. Machine-cast foam samples

Table XVIII shows the three formulations that were successfully used on the Polyair LIM machine. Several other formulations, with variations in amounts of catalyst and blowing agents, were evaluated but not included here. The quasi-prepolymer and the hardener components were maintained at a temperature of 145°F. The third stream remained at room temperature. The ratios used were 100 parts of hardener to 70 parts of quasi-prepolymer for all three formulations, and 2 parts of the third stream when formulation WF-14 was used.

One should note the similarity of formulation WF-11 with WF-13 and WF-14, and, also, WF-12 with WF-15. A foam slab sample was made with WF-13 with difficulty. One problem was that the Nitrosan began to decompose in the hardener tank, forming bubbles and perhaps causing a variation in the mole ratio. When WF-14 was attempted a good foam slab was made, but the Nitrosan in the third stream began to decompose at the entrance to the heated mixing head block. A foam slab was made using water, once the proper catalyst level was found, as shown in WF-15.

At this time, there were three formulations which could be used to make prototype boots once the formulations were optimized. WF-8 could be used with the prepolymer technique. This would mean

TABLE XVIII

MACHINE CAST FOAM SAMPLES

	WF-13 (Parts By Weight)	WF-14 (Parts By Weight)	WF-15 (Parts By Weight)
Quasi-Prepolymer Component			
PTMG/Hylene W Prepolymer	38.0	38.0	38.0
Hylene W	31.0	31.0	31.0
Hardener Component (Curing Agent)			
PTMG 2000	85.1	85.1	85.0
TMP	1.5	1.5	1.5
1,4 Butanediol	6.5	6.5	6.5
Water	–	–	0.15
SF 1079	2.0	3.5	3.0
White Pigment	1.0	–	1.0
DBTDL Catalyst	1.0	1.0	–
T-9 Catalyst	–	–	0.05
Dabco Catalyst	–	–	0.5
Nitrosan	2.0	–	–
Third Steam			
Nitrosan	–	1.0	–
White Pigment	–	1.0	–

a hand-cast boot since the necessary machinery was not readily available. The quasi-prepolymer technique could be used on the Polyair LIM machine to make a Nitrosan-blown boot (WF-14) and a water-blown boot (WF-15). To aid in optimizing the formulations, the samples made so far were analyzed further.

5. Foam compounding studies

Evaluations of foam formulations suitable for the white boot involved studies of upper foam formulations and outsole foam formulations. In keeping with the formulation and processing parameters established previously, several outsole foam formulations were made and evaluated. These formulations were hand-mixed but designed to be run on the Polyair LIM. Table XIX contains a list of the ten outsole formulations evaluated. Each formulation was expanded with water, cross-linked with TMP and 1,4 butanediol, and incorporated the PTMG 2000 polyol and a PTMG 2000/Hylene W prepolymer. Physical data of the compounds have shown that formulations No. 1 - 5 had excellent abrasion resistance (NBS index over 200).

Upper foam formulations using the quasi-prepolymer method were also evaluated. Table XX lists the upper foam formulations which were expanded with water. In trying to find the proper processing temperatures and catalyst levels, it was found that the foam tended to shrink after a room-temperature postcure of 2 - 24 hours. Thinking that the reason for shrinkage related to the foam being water-blown, formulations were tried using methylene chloride as an auxiliary blowing agent (see Table XXI). These foams also exhibited shrinkage after postcure. Table XXII lists formulations that were tried by varying the cross-linking agent (TMP) to prevent shrinkage. These foams again exhibited shrinkage after postcure.

Further attempts at eliminating the shrinkage problem with water-blown foam were unsuccessful, so work immediately proceeded toward evaluating Nitrosan as an expanding agent. Experiments performed to evaluate formulation using Nitrosan are listed in Table XXIII. The experiments were designed to produce a foam with the proper density and hardness necessary for the outsole. Initial work was performed at the lab bench to prepare for trials on the Polyair LIM. The results of this work has shown that trials on the LIM should be based on experiment #7.

The LIM had to be modified before the Nitrosan-expanded compound could be evaluated. The pigment stream was modified to dispense the Nitrosan/plasticizer dispersion and the temperature of the mixing head block was lowered to reduce the decomposition rate of the Nitrosan stream prior to compound mixing and injection.

TABLE XIX

WHITE BOOT OUTSOLE FORMULATIONS

(PARTS BY WEIGHT)

	1	2	3	4	5	6	7	8	9	10
PTMG 2000	100.0	98.0	97.0	97.0	100.0	75.0	75.0	75.0	75.0	75.0
TMP	2.6	2.6	2.6	2.6	2.6	1.0	2.0	3.0	4.0	5.0
1,4 ButaneDiol	5.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
H_2O	-	.2	.15	.05	.2	.15	.15	.15	.15	.15
DBTDL	5.0	10.0	10.0	10.0	8.0	.5	.5	.5	.5	.5
DC195	-	3.0	3.0	3.0	--	-	-	-	-	-
DC193	3.0	-	-	-	3.0	2.0	2.0	2.0	2.0	2.0
Hylene W Prepolymer	54.0	54.0	54.0	54.0	54.0	42.0	45.0	45.0	52.0	55.0
SHORE A HARDNESS	50	26	36	40	39	39	36	40	46	48
DENSITY	-	-	30	39	-	-	-	-	-	-
ABRASION INDEX	271	208	275	428	214	113	37.2	62.4	41.5	63.8

TABLE XX

WHITE BOOT UPPER FORMULATIONS (H_2O)
(PARTS BY WEIGHT)

	I	II	III	IV	V	VI	VII	VIII
PTMG 2000	100.0	100.0	100.0	100.0	50.0	50.0	50.0	45.0
Hylene W Prepolymer	54.0	54.0	54.0	54.0	41.0	41.0	41.0	41.0
TMP	2.6	2.6	2.6	2.6	1.3	1.3	1.3	1.3
DBTDL	5.0	10.0	15.0	10.0	6.0	4.0	2.0	2.0
1,4 Butanediol	5.5	5.5	5.5	5.5	2.8	2.8	2.8	3.1
H_2O	2.0	1.5	1.5	1.5	.80	.8	.8	.8
DC193	3.0	3.0	3.0	3.0	2.0	2.0	2.0	--
T-9 Catalyst	--	--	--	--	--	--	--	--
SF1079	--	--	--	--	--	--	--	2.0
DC190	--	--	--	--	--	--	---	--
DABCO catalyst	--	--	--	--	--	--	--	--
Prepolymer Temp	120°F	120°F	120°F	150°F	150°F	150°F	150°F	150°F
Hardner Temp	120°F	120°F	120°F	150°F	150°F	150°F	150°F	150°F
Cream Time	very long	very long	long	long	too fast	fast	good	good
Gel time	long	long	long	long	too fast	fast	good	good
Cell Structure	uniform	uniform	uniform	uniform	uniform	uniform	uniform	uniform
Comments	overblown, no curing	no curing Tin catalyst increased to reduce cure time	cure time too long - Tin catalyst still increased to reduce cure time	cure time still too long - initial reaction temperatures increased to induce curing	too much catalyst mole ratio changed to induce curing	reaction still too fast, foam collapses - catalyst lowered to slow reaction rate	foam collapses and shrinks catalyst level OK but foam shrinks	foam shrinks polymer long linkages increased so that shrinking would be reduced

TABLE XXI

WHITE BOOT UPPER FORMULATIONS (H_2O-METHYLENE CHLORIDE)

(PARTS BY WEIGHT)

	XIII	XIV	XV	XVI
PTMG 2000	50.0	50.0	50.0	50.0
Hylene W Prepolymer	30.0	30.0	30.0	30.0
TMP	1.0	1.0	1.0	1.0
DBTDL	2.0	1.7	1.7	1.7
1,4 ButaneDiol	3.0	3.0	3.0	3.0
H_2O	.1	.1	.1	.1
DC193	.5	.5	.5	-
SF1079	-	-	-	1
Prepolymer Temp	150°F	150°F	150°F	150°F
Hardner Temp	150°F	150°F	150°F	150°F
CH_2Cl_2	3.0	6.0	25.0	6.0
Comments	foam was fairly good but too dense	too much shrinkage - resulted in an attempt to lower density	excess CH_2Cl_2 was used in an attempt to get an open cell structure to reduce shrinking	SF1079 used in attempt to get open cell structure

TABLE XXII

WHITE BOOT UPPER FORMULATIONS (H_2O - TMP)

(PARTS BY WEIGHT)

	IX	X	XI	XII
PTMG 2000	50.0	50 .0	50.0	50.0
Hylene W Prepolymer	41.0	41.0	41.0	41.0
TMP	.3	0	.3	.3
DBTDL	2,0	2.0	-	2.0
1,4 ButaneDiol	2.8	2.8	2.8	2.8
H_2O	.8	.8	.8	.8
SF107	2.0	-	-	-
DC193	-	-	3.0	-
DC190	-	-	-	4.0
DABCO	-	1.0	1.0	-
Prepolymer Temp.	150°F	150°F	150°F	150°F
Hardner Temp	150°F	150°F	150°F	150°F
Cream Time	good	good	good	good
Gel Time	good	good	good	good
Cell Structure	good	good	good	poor
T-9	-	-	2g	-
Comments	excessive shrinking TMP reduced to lessen shrinkage and SF1079 added	excessive shrinking TMP reduced and Dabco added in hope of reducing shrinkage	excessive shrinking Tin catalyst changed in hope of reducing shrinkage	excessive shrinking overblown surfactant changed to reduce shrinking

TABLE XXIII

WHITE BOOT OUTSOLE FORMULATIONS (NITROSAN BLOWN)

(PARTS BY WEIGHT)

	1	2	3	4	5	6	7
PTMG 2000	-	-	-	-	13	13	13
1,4 Butanediol	3.0	3.0	3.0	3.0	3.0	3.0	3.0
TMP	1.5	1.5	1.5	1.5	1.5	1.5	1.5
T-12	.3	.2	.2	.2	.2	.2	.2
Nitrosan	4.0	4.0	3.0	2	2.2	2.1	3.0
LD 3056 4.28% NCO	100.0	100.0	100.0	100.0	98.2	98.2	98.2
Hylene W	-	-	-	-	1.82	1.82	1.82
Reaction Temperature	220°F	220°F	220°F	220°F	205°F	180°F	180°F
Mold Temperature	76°F	76°F	76°F	76°F	76°F	76°F	76°F
Comments	System is too fast. Foam cured before it could be poured into mold.	A very soft flexible foam was made	A denser foam than formulation #2 was made Amount of Nitrosan was changed in an attempt to produce a 25-30 lb/cu.ft. density foam.	A denser foam than formulation #2 was made Amount of Nitrosan was changed in an attempt to produce a 25-30 lb/cu. ft. density foam.	PTMG is added and reaction ratios are changed so that system is applicable to available processing equipment	Reaction temperature is lowered to reduce reaction rates. Foam density was 38 lbs/cu. ft.	Amount of Nitrosan is increased to lower density This is a suitable outsole material.

The outsole compound was injected into the test slab mold which was set at 100°F. The compound had a good cream time (25 seconds) and a good demold time (10 minutes). The excellent results of this trial established two precedents:

1. To our knowledge, this trial was the first time that a compound was successfully processed on a Polyair LIM using Nitrosan as the expanding agent.

2. This trial represented the first time a flexible foam had been machine-made from PTMG, hydrogenated MDI, and Nitrosan.

Three test slabs were submitted for testing and the results were as follows:

Test Slab	Shore A	Density	Polyair flexer (std 15,000 bends)
#1	76	43	failed at 6800 bends
#2	77	46	failed at 6600 bends
#3	81	52	failed at 4700 bends

The physical data of the slabs indicated that the compound had increased expansion thereby reducing the hardness and the density, and perhaps increasing the flexibility. Trials were made to evaluate the effect of (1) increased amounts of Nitrosan, and (2) reduced amounts of chain extender. The optimum formulations are discussed during the description of the prototypes (Table XXIV).

The Project Officer had suggested that a non-disc loring upper foam was not necessary if another type of upper foam could be made to satisfy the other physical requirements. This other type of upper foam could be masked with the outer skin to prevent discoloration of the foam or the discoloration showing through to the surface. To make this type of foam, evaluations of formulations using pure MDI were made. The optimum formulations using MDI (Table XXIV) are also discussed in the description of the prototypes.

B. Sprayed-On Outer Skin

Evaluation of sprayed-on outer skins were conducted in two directions (1) commercial urethane coating systems and (2) formulations based on PTMG and hydrogenated MDI using an airless spray gun for application. The first evaluation of a commercial, non-discoloring coating was made using a Midland Chemical coating system. This coating was being used by Uniroyal as a car bumper skin. Initial trials using black LIF boots (Contract #DAAG17-72-C-0058) have shown that the coating soaks into the upper foam to such a large degree that many applications would be necessary to produce a continuous film. Further attempts to spray a boot would necessitate sealing the upper foam cell structure with some type of topcoat prior to spraying the "bumper skin" coating.

The following are other commercial coating systems that were evaluated:

(1) Witcobond Y303 (Witco Chemical)

(2) Permuthane U-10-017 (Beatrice Chemical)

(3) Permuthane U-6366 (Beatrice Chemical)

(4) RO LS 159 (Millmaster Onyx Corp.)

(5) RO LS 73 (Millmaster Onyx Corp.)

All the above systems are one-component and produce non-discoloring, flexible **coatings** (from manufacturers' data sheets). An airless spray gun was used to apply the one-component coatings to the prototype boots. Since all the coatings were very similar, the RO LS 159 coating was chosen at random. The coating covered the boots evenly, but it did not hide any flaws or mold lines in the foam parts. After the coating dried properly, the adhesion of the film to the foam was poor. Because of time limitations, attempts to improve the outer skin could not be made.

C. Molds and Equipment

The prototype boots were to be fabricated using the Polyair LIM to cast into the size 10 boot molds developed during contract #DAAG17-72-C0058 black LIF boots. Since the Polyair injects material and the boot molds were designed for cast material, the LIM injector was modified with a new nozzle. The nozzle enabled the injected material to flow into the pour holes of the molds. The foam material could be placed in the mold easily in this manner; however, the Nitrosan expanding agent began to decompose in the heating mixing block.

To alleviate this problem, a modified Polyair casting machine was used. The machine is similar to the Polyair LIM except that the third stream (Nitrosan carrier) is separated from the main mixing block and cooled. The four prototype pair of boots submitted were fabricated on this machine.

D. Prototypes

Four pairs of prototype footwear were fabricated during Phase II. The prototype footwear have the following general characteristics:

1. Foam parts made using a modified Polyair casting machine.

2. The outsole foam and the upper foam were poured separately.

3. A standard cotton-backed, nylon sockling (from contract #DAAG17-72-C0058) was used.

4. Fabricated with size 10 black LIF boot molds.

5. Sprayed-on outer skin of RO-LS-159 one-component coating.

The following characteristics identify the various differences of the prototypes:

Prototype Pair #1

Outsole:

(a) formulation: PTMG 2000-HMDI-Nitrosan

(b) density: 35 to 40 lbs per cu. ft. - density gradient (integral skin)

(c) areas for evaluation: non-discoloring character
low temperature flexibility
wearability with density gradient
insulative properties

Upper:

(a) formulation: same as outsole

(b) density: 10 - 12 lbs per cu. ft. - uniform density

(c) areas for evaluation: non-discoloring character
low temperature flexibility
insulative properties

Prototype Pair #2

Outsole: the characteristics are the same as the outsoles of pair #1 except that a higher mold temperature cause the density to be lowered to 30-35 lbs per cu. ft. and the density gradient to be reduced.

Upper:

(a) formulation: PTMG 2000-MDI-Nitrosan (discolors on exposure to sunlight)

(b) density: 8-10 lbs per cu ft. - uniform density

(c) areas of evaluation: low temperature flexibility
insulative properties
degree of discoloration evidenced through the outer skin.

Prototype Pair #3

Outsole:

(a) formulation: PTMG 2000-HMDI-H_2O

(b) density: 35-40 lbs per cu. ft. - uniform density

(c) areas of evaluation: non discoloring character
low-temperature flexibility
insulative properties
wearability with uniform density

Upper: the characteristics are the same as the uppers of Pair #2 except lower mold temperatures increased the density to 10-12 lbs. per cu. ft. and caused a slight integral skin to form.

Prototype Pair #4

Outsole: the characteristics are the same as the outsoles of Pair #3

Upper: the characteristics are the same as the uppers of Pair #1 except lower mold temperatures increased the density to 12-14 lbs. per cu. ft. and caused a slight integral skin to form.

The above prototypes have been formulated and processed in such a way as to best exhibit the insulative, non-discoloring, flexibility and wear properties desired in an off-white insulated boot. The direction of any future work will be guided by the differences and variances noted in expanding agents, isocyanates, and mold temperatures.

TABLE XXIV

DATA APPLICABLE TO THE PROTOTYPE FOOTWEAR
(PARTS BY WEIGHT)

	PROTOTYPE #1		PROTOTYPE #2		PROTOTYPE #3		PROTOTYPE #4	
	outsole	upper	outsole	upper	outsole	upper	outsole	upper
	parts	parts	parts	parts	parts	parts	parts	parts
PTMG 2000	100	100	100	100	100	100	100	100
HMDI	34.7	34.7	34.7	-	36.8	-	36.8	34.7
1,4 Butanediol	5.9	5.9	5.9	3.7	5.1	3.7	5.1	5.9
TEA	1.4	1.4	1.4	1.5	1.8	1.5	1.8	1.4
DC-195	.4	.4	.4	.5	.1	.5	.1	.4
DABCO Wt	--	--	--	--	.5	--	.5	--
T-12	.04	.04	.04	.03	.2	.03	.2	.04
Water	--	--	--	--	.25	--	.25	--
Pigment	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Nitrosan	2.0	5.2	2.0	6.8	--	6.8	--	5.2
S-160	3.0	7.8	3.0	10.2	--	10.2	--	10.2
MDI	--	--	--	27.3	--	27.3	--	--
Mold Temp	RT	200°F	RT	190°F	RT	175°F	RT	175°F
Prepolymer Temp	206°F	206°F	206°F	205°F	180°F	205°F	180°F	206°F
Curative Temp	152°F	152°F	152°F	150°F	140°F	150°F	140°F	152°F
Cure Time	10min	10min	10min	10min	10min	10min	10min	10min
Post Cure	12hrs	12hrs	12hrs	12hrs	12hrs	12hrs	12hrs	12hrs
Post	@RT	@RT	@RT	@RT	@RT	@RT	@RT	@RT
*density	45.0	11.0	45.0	10.0	45.0	15.0	50.0	15.0
compression set (50%)	7.4	7.4	7.4	10.0	6.0	8.5	6.0	7.4
water absorption-% by vol.	.4	6.5	.4	7.5	.4	6.5	.4	6.5
water absorption-% by wt.	1.2	29.2	1.2	34.0	1.2	29.0	1.2	29.2
hardness, Shore A	65.0	--	65.0	--	70.0		70.0	--
NBS abrasion index	12.0	--	12.0	--	35.0	--	35.0	--

*physical data obtained from test slabs approximating boot parts

Section III - Conclusions

1. A non-discoloring, cold-dry boot has been made on a liquid-injection molding machine.

2. Water-blown urethane foam was best suited for outsole application.

3. The Nitrosan expanding agent was used to fabricate both outsole foam and upper foam. The Nitrosan was successfully processed on a modified Polyair casting machine.

4. The feasibility of a sprayable, one-component outer skin was not completely proven. A good quality outer skin has not yet been found.

5. A Nitrosan-blown, MDI type upper foam can be used, but it will yellow on exposure to sunlight.

6. Reproducibility of good quality white boots must be proven.

APPENDIX A

Data Applicable to the Computerized Study
of Polybutadienediol based Formulations

TABLES A-I through A-X

TABLE A-I

PREDICTED TENSILE STRENGTH VALUES (PSI)

	POLY BD R 15 M						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	772	160	1045	535	600	75	470
ISONOL C 100	1050	438	1323	813	878	353	748
1,4-BD	960	348	1233	723	788	263	658
1,6-HD	750	138	1023	513	578	53	448
TMHD	890	278	1163	653	718	193	588

	POLY BD R 45 M						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	960	348	1233	723	788	263	658
ISONOL C 100	1238	627	1512	1002	1067	542	937
1,4-BD	1148	537	1422	912	977	452	847
1,6-HD	938	327	1212	702	767	242	637
TMHD	1078	467	1352	842	907	382	777

	POLY BD CS 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	1088	477	1362	852	917	392	787
ISONOL C 100	[illegible]	755	1640	1130	1195	670	1065
1,4-BD	1277	655	1550	1040	1105	580	975
1,6-HD	1067	455	1340	830	895	370	765
TMHD	1207	595	1480	970	1035	510	905

	POLY BD CN 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	630	18	903	393	458	*	328
ISONOL C 100	908	297	1182	672	737	212	607
1,4-BD	818	207	1092	582	647	122	517
1,6-HD	608	*	882	37.2	437	*	307
TMHD	748	137	1022	512	577	52	447

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
Poly BD CS 15 - Hydroxy Terminated Styrene/Butadiene Copolymer
Poly BD CN-15 - Hydroxy Terminated Acrylonitrile/butadiene Copolymer
NAC H12 - Hydrogenated MDI (70% Trans)
Iso 143 L - Modified MDI
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI mixture (replaces Desmodur HL)

Des N - Modified HDI
DDI 1410 - Dimer Diisocyanates
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethenol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol
TMHD - Trimethylhexanediol

TABLE A-II

PREDICTED PER CENT ELONGATION VALUES

	POLY BD R 15 M						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	1630	50	200	47	[illegible]	200	130
ISONOL C 100	180	77	217	63	27	217	147
1,4-BD	232	128	268	115	78	268	198
1,6-HD	210	107	247	93	56	247	377
TMHD	230	127	267	113	77	267	197

	POLY BD R 45 M						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	300	197	337	183	147	337	267
ISONOL C 100	317	213	253	200	163	353	283
1,4-BD	368	265	405	252	215	405	335
1,6-HD	347	243	383	230	193	383	313
TMHD	367	263	403	250	213	403	333

	POLY BD CS 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	297	193	333	180	143	333	263
ISONOL C 100	313	210	350	197	[illegible]	350	280
1,4-BD	365	262	402	248	212	402	332
1,6-HD	343	240	380	226	190	380	310
TMHD	363	260	48[illegible]	[illegible]	210	48[illegible]	330

	POLY BD CN 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	350	247	387	233	197	387	317
ISONOL C 100	367	263	403	250	213	403	333
1,4-BD	418	315	455	302	265	455	385
1,6-HD	397	293	433	280	243	433	363
TMHD	416	313	453	300	263	453	383

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
Poly BD CS15 - Hydroxy Terminated Styrene/Butadiene Copolymer
Poly BD CN-15 - Hydroxy Terminated Acrylonitrile/butadiene Copolymer
NAC H12 - Hydrogenated MDI (70% Trans)
Iso 143L - Modified MDI
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI mixture (replaces Desmodur HL)
DES N - Modified HDI
DDI 1410 - Dimer Diisocyanates
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4 - Butanediol
1,6-HD - 1,6 - Hexanediol
TMHD - Trimethylhexanediol

TABLE A-III

PREDICTED DIE C TEAR VALUES (LBS./IN.)

	POLY BD R 15 M							POLY BD R 45 M							POLY BD CS 15							POLY BD CN 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	243	35	175	55	55	25	75	285	77	217	97	97	67	117	262	37	213	93	93	63	113	205	*	337	17	17	*	37
ISONOL C 100	325	117	257	137	137	107	157	367	158	298	178	178	148	198	363	155	295	175	175	145	195	287	78	218	98	98	68	118
1,4-BD	253	45	185	65	65	35	85	295	87	227	107	107	76	127	292	83	223	103	103	73	123	215	*	147	27	27	*	47
1,6-HD	215	*	147	27	27	*	47	257	48	188	68	68	38	88	253	45	185	65	65	35	85	177	*	108	*	*	*	*
TMHD	225	17	157	37	37	*	57	267	58	198	78	78	48	98	263	55	195	75	75	45	95	187	*	118	*	*	*	18

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
Poly BD CS 15 - Hydroxy Terminated Styrene/Butadiene Copolymer
Poly BD CN 15 - Hydroxy Terminated Acrylonitrile/butadiene Copolymer
NAC H12 - Hydrogenated MDI (70% Trans)
Iso 143L - Modified MDI
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI mixture (replaces Desmodur HL)
DES N - Modified HDI
DDI 1410 - Dimer Diisocyanates
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis (2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol
TMHD - Trimethylhexanediol

TABLE A-IV

PREDICTED GERMAN T_g VALUES (°C.)

	POLY BD R 15 M							POLY BD R 45 M							POLY BD CS 15							POLY BD CN 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	-55	-70	-62	-59	-70	-27	-67	-54	-59	-51	-48	-59	-16	-56	-34	-40	-32	-29	-40	+3	-37	-22	-27	-19	-17	-27	+16	-24
ISONOL C 100	-51	-56	-48	-46	-56	-13	-53	-40	-46	-38	-35	-46	- 3	-43	-21	-26	-18	-15	-26	+17	-23	- 8	-14	- 6	- 3	-14	+29	-11
1,4-BD	-63	-69	-61	-58	-69	-26	-66	-53	-58	-50	-47	-58	-15	-55	-33	-38	-30	-28	-38	+ 5	-35	-21	-26	-18	-15	-26	+17	-23
1,6-HD	-65	-70	-62	-60	-70	-27	-67	-54	-60	-52	-49	-60	-17	-57	-35	-40	-32	-29	-40	+ 3	-37	-22	-28	-20	-17	-28	+15	-25
TMHD	-40	-45	-37	-35	-45	- 2	-42	-29	-35	-27	-24	-35	+ 8	-32	-10	-15	- 7	- 4	-15	+28	-12	-3	- 3	+ 5	+ 8	- 3	+40	0

KEY:

Poly BD R15 M	-	Hydroxy Terminated Polybutadiene
Poly BD R45 M	-	Hydroxy Terminated Polybutadiene
Poly BD CS 15	-	Hydroxy Terminated Styrene/Butadiene Copolymer
POly BD CN-15	-	Hydroxy Terminated Acrylonitrile/butadiene Copolymer
NAC H12	-	Hydrogenated MDI (70% Trans)
Iso 143L	-	Modified MDI
HYLN W	-	Hydrogenated MDI (more than 30% C's)
Mon HC	-	HDI - TDI mixture (replaces Desmodur HL)
DES N	-	Modified HDI
DDI 1410	-	Dimer Diisocyanates
LDI	-	Lysine Methyl Ester Diisocyanates
CHDM	-	1,4-Cyclohexanedimethanol
Isonol C100	-	N,N-bis(2 hydroxypropyl) Aniline
1,4-BD	-	1,4-Butanediol
1,6-HD	-	1,6-Hexanediol
TMHD	-	Trimethylhexanediol

TABLE A-V

PREDICTED GERMAN T_{10} VALUES (°C.)

	POLY BD R 15 M							POLY BD R 45 M							POLY BD CS 15							POLY BD CN 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	-69	-70	-69	-67	-70	-34	-70	-68	-69	-68	-66	-69	-33	-69	-43	-43	-42	-40	-43	- 7	-43	-32	-33	-32	-30	-33	+ 3	-33
ISONOL C 100	-66	-67	-66	-64	-67	-31	-67	-65	-65	-64	-62	-65	-29	-65	-39	-40	-39	-37	-40	- 4	-40	-29	-29	-28	-26	-29	+ 7	-29
1,4-BD	-68	-69	-68	-66	-69	-33	-69	-67	-68	-67	-65	-68	-32	-68	-42	-42	-41	-39	-42	- 6	-42	-31	-32	-31	-29	-32	+ 4	-32
1,6-HD	-70	-71	-70	-68	-71	-35	-71	-69	-69	-68	-66	-69	-33	-69	-43	-44	-43	-41	-44	- 8	-44	-33	-33	-32	-30	-33	+ 3	-33
TMHD	-57	-58	-57	-55	-58	-22	-58	-56	-59	-55	-53	-56	-20	-56	-30	-31	-30	-28	-31	- 5	-31	-20	-20	-19	-17	-20	+16	-20

KEY:

Poly BD R15 M	-	Hydroxy Terminated Polybutadiene
Poly BD R45 M	-	Hydroxy Terminated Polybutadiene
Poly BD CS15	-	Hydroxy Terminated Styrene/Butadiene Copolymer
Poly BD CN-15	-	Hydroxy Terminated Acrylonitrile/butadiene Copolymer
NAC H12	-	Hydrogenated MDI (70% Trans)
Iso 143L	-	Modified MDI
HYLN W	-	Hydrogenated MDI (more than 30% Cis)
Mon HC	-	HDI - TDI mixture (replaces Desmodur HL)
DES N	-	Modified HDI
DDI 1410	-	Dimer Diisocyanates
LDI	-	Lysine Methyl Ester Diisocyanates
CHDM	-	1,4-Cyclohexanedimethanol
Isonol C100	-	N,N-bis(2 hydroxypropyl) Aniline
1,4-BD	-	1,4-Butanediol
1,6-HD	-	1,6-Hexanediol
TMHD	-	Trimethylhexanediol

TABLE A-VI

PREDICTED GERMAN T_{100} VALUES (°C.)

	POLY BD R 15 M							POLY BD R 45 M							POLY BD CS 15							POLY BD CW 15						
	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI	NAC H12	ISO 143L	HYLN W	MON HC	DES N	DDI 1410	LDI
CHDM	-70	-70	-70	-70	-70	-62	-70	-70	-70	-70	-70	-70	-62	-70	-57	-57	-57	-57	-57	-49	-57	-48	-48	-48	-48	-48	-40	-48
ISONOL C 100	-70	-70	-70	-70	-70	-62	-70	-70	-70	-70	-70	-70	-62	-70	-57	-57	-57	-57	-57	-49	-57	-48	-48	-48	-48	-48	-40	-48
1,4-BD	-70	-70	-70	-70	-70	-62	-70	-70	-70	-70	-70	-70	-62	-70	-57	-57	-57	-57	-57	-49	-57	-48	-48	-48	-48	-48	-40	-48
1,6-BD	-70	-70	-70	-70	-70	-62	-70	-70	-70	-70	-70	-70	-62	-70	-57	-57	-57	-57	-57	-49	-57	-48	-48	-48	-48	-48	-40	-48
TMHD	-70	-70	-70	-70	-70	-62	-70	-70	-70	-70	-70	-70	-62	-70	-57	-57	-57	-57	-57	-49	-57	-48	-48	-48	-48	-48	-40	-48

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
Poly BD CS 15 - Hydroxy Terminated Styrene/Butadiene Copolymer
Poly BD CN-15 - Hydroxy Terminated Acrylonitrile/butadiene Copolymer
NAC H12 - Hydrogenated MDI (70% Trans)
Iso 143L - Modified MDI
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI mixture (replaces Desmodur HL)

DES N - Modified HDI
DDI 1410 - Dimer Diisocyanates
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol
TMHD - Trimethylhexanediol

TABLE A-VII

TENSILE STRENGTH (PSI) OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLY BD R 15 M		POLY BD R 45 M				
	MAC H12	HYLN W	MAC H12	HYLN W	MON HC	DES N	LDI
CHDM			960	1233			
ISONOL C 100		1323	1238	1512			937
1,4-BD	960	1233	1148	1422	912	977	847
1,6-HD		1023	938	1212			

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
MAC H12 - Hydrogenated MDI (70% Trans)
Iso 143L - Modified MDI
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI mixture (replaces Desmodur HL)
DES N - Modified HDI
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol

TABLE A-VIII

PERCENT ELONGATION OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLY BD R15 M							POLY BD R 45 M																				
	NAC H12		HYLN W					NAC H12		HYLN W	MON HC	DES N		LDI														
CHDM								300		337																		
ISONOL C 100			217					317		253				283														
1,4-BD	232		268					368		405	252	215		325														
1,6-HD			247					347		383																		

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
NAC H12 - Hydrogenated MDI (70% Trans)
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI Mixture (replaces Desmodur HL)

DES N - Modified HDI
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxylpropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol

TABLE A-IX

GERMAN T_5 OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLY BD R 15 M							POLY BD R 45 M						
	NAC H12		HYLN W					NAC H12		HYLN W	MON HC	DES N		LDI
CHDM								-54		-51				
ISONOL C 100			-48					-40		-38				-43
1,4-BO	-63		-61					-53		-50	-47	-58		-55
1,6-HD			-62					-54		-52				

KEY:

Poly BD R15 M - Hydroxy Terminated Polybutadiene
Poly BD R45 M - Hydroxy Terminated Polybutadiene
NAC H12 - Hydrogenated MDI (70% Trans)
HYLN W - Hydrogenated MDI (more than 30% Cis)
MON HC - HDI - TDI mixture (replaces Desmodur HL)
DES N - Modified HDI
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BO - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol

TABLE A-X

GEHMAN T_{10} OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLY BD R 15 M							POLY BD R 45 M																				
	NAC H12		HYLN W					NAC H12		HYLN W	MON HC	DES N		LDI														
CHDM								-68		-68																		
ISONOL C 100			-66					-65		-64				-65														
1,4-BD	-68		-68					-67		-67	-65	-68		-68														
1,6-HD			-70					-69		-68																		

KEY:

Poly BD R 15 M - Hydroxy Terminated Polybutadiene
Poly BD R 45 M - Hydroxy Terminated Polybutadiene
NAC H12 - Hydrogenated MDI (70% Trans)
HYLN W - Hydrogenated MDI (more than 30% Cis)
Mon HC - HDI - TDI mixture (replaces Desmodur HL)
DES N - Modified HDI
LDI - Lysine Methyl Ester Diisocyanates
CHDM - 1,4-Cyclohexanedimethanol
Isonol C100 - N,N-bis(2 hydroxypropyl) Aniline
1,4-BD - 1,4-Butanediol
1,6-HD - 1,6-Hexanediol

APPENDIX B

Data Applicable to the Computerized Study of PTMG based Formulations

TABLES B-I through B-VII

TABLE B-I

RESTRICTION: TENSILE STRENGTH ≥ 800 PSI

	POLYMEG 2000		POLYMEG 1000		POLYMEG 1500				POLYMEG 650	POLYMEG 3000			
	HYLN W	MDI	HYLN W	MDI	HYLN W	MDI	DES N	TDI	HYLN W	HYLN W	MDI	DES N	TDI
MDA* MOCA**	4072	1935	3469	1332	4550	2313	886	1080	2100	4385	2249	822	1016
1,4-BD	1980		1378		2358					2293			

*MDA to be used with HYLN W and DES N. **MOCA to be used with MDI and TDI.

KEY:

Polymeg 2000	- Polytetramethylene Ether Glycol (2000 mol. wt.)	DES N	- Modified HDI
Polymeg 1000	- Polytetramethylene Ether Glycol (1000 mol. wt.)	TDI	- Tolylene diisocyanate
Polymeg 1500	- Polytetramethylene Ether Glycol (1500 mol. wt.)	MDA	- p,p - Methylene dianiline
Polymeg 650	- Polytetramethylene Ether Glycol (650 mol. wt.)	MOCA	- 3,3'-Dichloro-4,4'- diamine-diphenylmethane
Polymeg 3000	- Polytetramethylene Ether Glycol (3000 mol. wt.)	CHDM	- 1,4 - Cyclohexanedimethanol -
HYLN W	- Hydrogenated MDI (more than 30% cis)	1,4-BD	- 1,4 - Butenediol
MDI	- 4,4' - diphenylmethane diisocyanate	ISONOL C100	- N,N - bis (2 hydroxypropyl) Aniline

TABLE B-II

RESTRICTION: PERCENT ELONGATION ≥ 200%

	POLYMEG 2000				POLYMEG 1000				POLYMEG 1500				POLYMEG 650				POLYMEG 3000			
	HYLN W	MDI	DES N	TDI	HYLN W	MDI	DES N	TDI	HYLN W	MDI	DES N	TDI	HYLN W	MDI	DES N	TDI	HYLN W	MDI	DES N	TDI
MDA* MOCA**	596	796		1033	462	662		899	505	705		943	210	410		647	590	790		1027
CHDM	1000	1200	594	1437	866	1066	460	1303	909	1109	503	1346	614	814	208	1052	994	1194	587	1431
1,4-BD	770	970	364	1203	636	836	230	1074	679	879	273	1116	384	584		822	764	964	358	1201
ISONOL C 100	1000	1200	594	1438	866	1066	460	1304	909	1109	503	1346	614	814	208	1052	994	1194	588	1431

*MDA to be used with HYLN W and DES N. **MOCA to be used with MDI and TDI

KEY:

- Polymeg 2000 - Polytetramethylene Ether Glycol (2000 mol. wt.)
- Polymeg 1000 - Polytetramethylene Ether Glycol (1000 mol. wt.)
- Polymeg 1500 - Polytetramethylene Ether Glycol (1500 mol. wt.)
- Polymeg 650 - Polytetramethylene Ether Glycol (650 mol. wt.)
- Polymeg 3000 - Polytetramethylene Ether Glycol (3000 mol. wt.)
- HYLN W - Hydrogenated MDI (more than 30% cis)
- MDI - 4,4' - Diphenylmethane diisocyanate
- DES N - Modified HDI
- TDI - Tolylene diisocyanate
- MDA - p,p - Methylene dianiline
- MOCA - 3,3'-Dichloro-4,4'-diamino-**diphenylmethane**
- CHDM - 1,4 - Cyclohexanedimethanol
- 1,4-BD - 1,4-Butanediol
- ISONOL C100 - N,N - bis (2 hydroxypropyl) Aniline

TABLE B-III

100% MODULUS (lbs.) OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLYMEG 2000		POLYMEG 1500		POLYMEG 3000	
	HYLN W	MDI	HYLN W	MDI	HYLN W	MDI
MDA * MOCA**	365	232		417		229
1,4-BD	222		407		219	

*MDA to be used with HYLN W and DES N. ** MOCA to be used with MDI and TDI

KEY:
Polymeg 2000 - Polytetramethylene Ether Glycol (2000 mol. wt.)
Polymeg 1500 - Polytetramethylene Ether Glycol (1500 mol. wt.)
Polymeg 3000 - Polytetramethylene Ether Glycol (3000 mol. wt.)
HYLN W - Hydrogenated MDI (more than 30% cis)
MDI - 4,4' - diphenylmethane diisocyanate
MDA - p,p - Methylene dianiline
MOCA - 3,3'-Dichloro-4,4'-diamino-diphenylmethane
1,4-BD - 1,4-Butanediol

TABLE B-IV

TENSILE STRENGTH (PSI) OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLYMEG 2000		POLYMEG 1500		POLYMEG 3000	
	HYLN W	MDI	HYLN W	MDI	HYLN W	MDI
MDA* MOCA**	4072	1935		2313		2249
1,4-BD	1980		2358		2293	

*MDA to be used with HYLN W and DES N. **MOCA to be used with MDI and TDI.

KEY:
Polymeg 2000 - Bolytetramethylene Ether Glycol (2000 mol.wt.)
Polymeg 1500 - Polytetramethylene Ether Glycol (1500 mol.wt.)
Polymeg 3000 - Polytetramethylene Ether Glycol (3000 mol.wt.)
HYLN W - Hydrogenated MDI (more than 30% cis)
MDI - 4,4' - diphenylmethane diisocyanate
MDA - p,p - Methylene dianiline
MOCA - 3,3'-Dichloro-4,4'-diamino-diphenylmethane
1,4-BD - 1,4-Butanediol

TABLE B-V

PERCENT ELONGATION OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLYMEG 2000		POLYMEG 1500		POLYMEG 3000	
	HYLN W	MDI	HYLN W	MDI	HYLN W	MDI
MDA* MOCA**	596	796		705		790
1,4-BD	770		679		764	

*MDA to be used with HYLNW and DES N. **MOCA to be used with MDI and TDI

KEY:
- Polymeg 2000 - Polytetramethylene Ether Glycol (2000 mol.wt.)
- Polymeg 1500 - Polytetramethylene Ether Glycol (1500 mol.wt.)
- Polymeg 3000 - Polytetramethylene Ether Glycol (3000 mol.wt.)
- HYLN W - Hydrogenated MDI (more than 30% cis)
- MDI - 4,4'-diphenylmethane diisocyanate
- MDA - p,p-Methylene dianiline
- MOCA - 3,3'-Dichloro-4,4'-diamino-diphenylmethane
- 1,4-BD - 1,4-Butanediol

TABLE R-VI

DIE C TEAR VALUES (lbs./in.) OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLYMEG 2000 HYLN W	POLYMEG 2000 MDI	POLYMEG 1500 HYLN W	POLYMEG 1500 MDI	POLYMEG 3000 HYLN W	POLYMEG 3000 MDI
MDA* MOCA**	457	328		381		318
1,4-BD	318		[illegible]		308	

*MDA to be used with HYLN W and DES N. **MOCA to be used with MDI and TDI.

KEY:
- Polymeg 2000 - Polytetramethylene Ether Glycol (2000 mol.wt.)
- Polymeg 1500 - Polytetramethylene Ether Glycol (1500 mol.wt.)
- Polymeg 3000 - Polytetramethylene Ether Glycol (3000 mol.wt.)
- HYLN W - Hydrogenated MDI (more than 30% cis)
- MDI - 4,4'-diphenylmethane diisocyanate
- MDA - p,p-Methylene dianiline
- MOCA - 3,3'-Dichloro-4,4'-diamine-diphenylmethane
- 1,4-BD - 1,4-Butanediol

TABLE B-VII

GERMAN T_5 VALUES (°C) OF COMBINATIONS MEETING ALL RESTRICTIONS

	POLYMEG 2000		POLYMEG 1500		POLYMEG 3000	
	HYLN W	MDI	HYLN W	MDI	HYLN W	MDI
MDA* MOCA**	-35.7	-48.0		-43.3		-42.3
1,4-BD	-43.7		-39.0		-38.0	

*MDA to be used with HYLN W and DES N. **MOCA to be used with MDI and TDI.

KEY:
- Polymeg 2000 - Polytetramethylene Ether Glycol (2000 mol.wt.)
- Polymeg 1500 - Polytetramethylene Ether Glycol (1500 mol.wt.)
- Polymeg 3000 - Polytetramethylene Ether Glycol (3000 mol.wt.)
- HYLN W - Hydrogenated MDI (more than 30% cis)
- MDI - 4,4'-diphenylmethane diisocyanate
- MDA - p,p - Methylene dianiline
- MOCA - 3,3'-Dichloro-4,4'-diamino-diphenylmethane
- 1,4-BD - 1,4-Butanediol

APPENDIX C

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LIST OF MATERIALS

MATERIAL (TRADE NAME)	CHEMICAL NAME	SOURCE
1,4-Butanediol	1,4-Butanediol	GAF Corp.
CHDM	1,4-cyclohexanedimethanol	Eastman Chem.
cyclohexanone	cyclohexanone	Fisher Scientific Co.
Dabco	triethylenediamine	Dow Corning Corp.
DC195, DC193	silicone surfactant	Dow Corning Corp.
DDI 1410	dimer diisocyanate	General Mills Chem.
Desmodur N	modified HDI	Mobay Chemical Co.
dimethyl benzene	dimethyl benzene	Fisher Scientific Co.
1,6-hexanediol	1,6-hexanediol	Celanese Chem.
Hylene W	hydrogenated MDI	E.I. DuPont DeNemours & Co., Inc.
Isonate 143L	modified MDI	Upjohn Co.
Isonol C100	N,N-bis(2 hydroxylpropyl) aniline	Upjohn Co.
LDI	lysine methyl ester diisocyanate	Mobay Chemical Co.
MDA	p,p-methylene dianiline	Upjohn Co.
MDI	4,4' diphenylmethane diisocyanate	Mobay Chemical Co.
methylene chloride	methylene chloride	Hubbard-Hall Chemical
MOCA	3,3'-dichloro-4,4'-diamino-diphenylmethane	E.I. DuPont DeNemours & Co., Inc.

Mondur HC	HDI-TDI mixture	Mobay Chemical Co.
Nacconate H12	hydrogenated MDI	Allied Chemical Co.
Nitrosan	N,N'-dinitroso- N,N' dimethyl terephthalamide	E.I. DuPont DeNemours & Co., Inc.
Poly BD R15M	hydroxy terminated polybutadiene	Arco Chem.
Poly BD R45M	hydroxy terminated polybutadiene	Arco Chem.
Poly BD CS15	hydroxy terminated polybutadiene-styrene-copolymer	Arco Chem.
Poly BD CN15	hydroxy Terminated polybutadiene-acrylonitrile-copolymer	Arco Chem.
Polymeg 3000	polytetramethylene ether glycol	Quaker Oats Chem.
Polymeg 2000	polytetramethylene ether glycol	Quaker Oats Chem.
Polymeg 1500	polytetramethylene ether glycol	Quaker Oats Chem.
Polymeg 650	polytetramethylene ether glycol	Quaker Oats Chem.
Santicizer S-160	butyl benzyl phthalate	Monsanto Chemical Co.
SF-1079	silicone surfactant	General Electric Co.
TEA	triethanol amine	Union Carbide Co.
TDI	tolylene diisocyanate	Upjohn Co.
TMHD	trimethylhexanediol	Hugo Stinnes Chem.
TMP	trimethanol propane	Celanese Chem.
T-9	stannous octoate	M&T Chemical Co.
T-12	dibutyl tin dilaurate	M&T Chemical Co.